Milan Melník, Peter Mikuš, Clive E. Holloway

Crystallographic and structural characterization of heterometallic platinum complexes
Part X. Heteropolynuclear pt complexes

Abstract: This review covers heteropolynuclear platinum complexes. There are over sixty examples with heterometal atoms as partners including non-transition metals, K, Cs, Mg, Ca, Sr, Tl, Sn, Pb, Zn, Cd, and transition metals: Cu, Ag, Fe, Co, Ni, Rh and Pd. In addition, there are examples for the lanthanides, Eu and Yb. The most common are Ag (x16) and K (x14). The predominant geometries for Pt(II) is square-planar and for Pt(IV) is octahedral. The overall structures are complex. In spite of the wide variety of heterometal atoms partners of platinum, there is “real” Pt-M bonds only with silver, ranging from 2.678 to 2.943(1) Å (ave 2.855 Å). The mean Pt-Pt bond distance is 2.869 Å.

Keywords: structure, heteropolynuclear, platinum, classify, analyze

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1 Introduction

There has been increasing interest in recent years in the synthesis of heterometallic compounds. Structural details have attracted much attention from the viewpoint of nano-scale science, supramolecular chemistry, crystal engineering and solid state chemistry properties. Weak interactions such as hydrogen-bonding, charge transfer interactions and weak metal-metal heteronuclear bonding, along with strong chemical bonds, have been found to be important in such systems. The heterometallic platinum complexes are no exception. Up to the end of the year 2000 there have been numerous published structural studies on heterometallic platinum complexes (clusters). We have already analyzed and discussed the factors which can lead to better understanding of the stereochemical interactions in the heterobinuclear to heterooligonuclear platinum clusters [1-9]. This review article presents a brief survey on the crystal and structural data of heteropolynuclear platinum complexes. This review together with its precursors [1-9], represents the first comprehensive overview of almost one thousand and five hundred heterometallic platinum complexes (clusters) for which the structures have been established by X-ray crystallographic techniques.

2 Heteropolynuclear Pt complex

Due to complex nature of the structures of these heteropolynuclear complexes, the systems have been classified according to the coordination number of the platinum. The complexes have been listed and referenced in order of increasing coordination number, increasing complexity of the inner coordination sphere, and increasing atomic number of the principle coordinating donor.

2.1 Complexes with PtO₄ and PtN₄ chromophores

There are over twenty heteropolynuclear platinum complexes with PtO₄ and PtN₄ chromophores for which the crystallographic and structural parameters are gathered in Table 1. The structure of monoclinic colorless [Pt(µ-acac),Ag(µ-CF₃SO₃),Ag(H₂O)] [10] can be described as a 2-D sheet comprised of three units, {Ag(H₂O)}₂[Ag(CF₃SO₃)]
Table 1: Crystallographic and structural data for heteropolynuclear platinum complexes with PtO₄ and PtN₄ chromophores.

| COMPOUND | Cr. sys. | Sp.gr. | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | L-M-L [°] | Ref |
|----------|----------|--------|-------|-------|-------|-------|-------|-------|------------|--------|--------|-----------|-----|
| [Pt(µ-acac)₂Ag.₃(µ-CF₃SO₃)₂Ag.₃(H₂O)]₂ | m | m | 13.039(7) | 12.287(3) | 102.90(2) | 102.04(1) | 115.17(3) | 43.58(4) | PtO₄ | acacO,1.978(9,12) | acacO,2.53(1,6) | H₂O,2.28(1) | acacO,2.43(1,9) | 10 |
| [Pt(µ-ox)₂Ag.₂(H₂O)₂] | m | m | 9.745(2) | 7.913(1) | 117.05(1) | 115.81(9) | 102.32(17) | 93.7(5) | PtO₄ | oxO,2.003(4,0) | oxO,2.595(6,37) | H₂O,2.463(9,39) | not given | 10 |
| Rb₁.₆₇Pt(µ-ox)₂.1.₅H₂O | tr | C₂/m | 12.690(10) | 17.108(14) | 11.357(3) | 99.54(9) | 115.81(9) | 102.32(17) | PtO₄ | RbO₇ | RbO₈ | oxO,2.01(2,4) | 11 |
| K₁.₆₇Pt(µ-ox)₂.1.₂H₂O | tr | C₂/m | 9.749(9) | 11.403(18) | 10.694(3) | 99.54(9) | 115.81(9) | 102.32(17) | PtO₄ | KOn | oxO,2.00(1) | not given | 12 |
| Ni₁.₈₄Pt(µ-ox)₂.6H₂O | m | C₂/n | 7.086(7) | 14.085(7) | 127.0(1) | 127.3(1) | 100.59(4) | 111.73(4) | PtO₄ | NiO₆ | oxO,2.00(1) | not given | 13 |
| Co₁.₈₃Pt(µ-ox)₂.6H₂O | m | C₂/m | 14.379(2) | 16.501(2) | 5.682(1) | 93.7(5) | 115.81(9) | 102.32(17) | PtO₄ | CoO₆ | oxO,2.003(7) | 2.024(8) | H₂O,2.138(7) | 2.243(9,16) | 15 |
| Mg₁.₈₂Pt(µ-ox)₂.₅.₅H₂O | m | Cccm | 16.56(1) | 14.27(1) | 5.70(1) | 93.7(5) | 115.81(9) | 102.32(17) | PtO₄ | MgO₆ | oxO,1.98(3) | 2.01(3) | H₂O,2.135(5) | 2.23(5) | 16 |
| Ca⁻¹⁻⁻Pt(µ-ox)₂.3.H₂O | m | C₂/m | 9.33(3) | 10.72(3) | 6.36(1) | 93.7(5) | 115.81(9) | 102.32(17) | PtO₄ | CaO₂ | oxO,2.00(1) | not given | 17 |
| [Cu(en)₂]⁻¹⁻⁻Pt(µ-ox)₂.2H₂O | m | C₂/m | 21.52(4) | 24.14(4) | 14.16(4) | 93.7(5) | 115.81(9) | 102.32(17) | PtO₄ | CuN₂O₂ | oxO,2.00(2) | not given | 18 |
| [Ni(oaoH₂)₂]⁻⁻⁻Pt(µ-ox)₂.2H₂O | m | m | 3.673(1) | 9.418(6) | 12.25(8) | 94.01(2) | 95.11(2) | 111.73(4) | PtO₄ | CuN₂O₂ | oxO,2.007(4) | 2.019(4) | N,N,86.4(7) | 19 |
| {Ni(oao)}⁻⁻⁻Pt(µ-ox)₂.2H₂O | m | m | 13.622(4) | 13.417(4) | 92.14(2) | 94.01(2) | 95.11(2) | 111.73(4) | PtO₄ | CuN₂O₂ | oxO,2.007(4) | 2.019(4) | N,N,86.4(7) | 20 |
Table 1: Crystallographic and structural data for heteropolynuclear platinum complexes with PtO₄ and PtN₄ chromophores.

| COMPOUND (colour) | Cr. sys. | Sp.gr. | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | L-M-L [°] | Ref |
|------------------|----------|--------|-------|-------|-------|-------|-------|-------|-------------|---------|---------|-------------|-----|
| K₂Pt(µ-memal)₂. 2H₂O (red) | tr       | Pim    | 4.059(1) | 9.107(2) | 10.111(2) | 98.49(1) | 101.28(1) | 101.84(1) | PtO₄       | 0.200(4) | 2.010(4) |          | 21  |
|                  |          | 1      |       |       |       |       |       |       | KO          |         |         |             |     |
| K₂Pt(µ-piv) 3thf (pale brown) | m        | P2₁/n  | 13.029(3) | 15.948(4) | 20.253(5) |       |       |       | PtO₄       | 0.209(7,4)| 2.018(6,4)|             | 22  |
|                  |          | 4      |       |       |       |       |       |       | KO          |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η²-meu)₂Ag(NO₃)₂(H₂O)] | or     | Pna₂   | 13.206(6) | 7.238(9) | 22.65(10) |       |       |       | PtO₄       |         |         |             |     |
| NHDMe)Ag(  | |       |       |       |       |       |       |       |             |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 4      |       |       |       |       |       |       |             |         |         |             |     |
| cis-[(NH₄)₂Pt(µ-η²-NHCOMe)₂Ag(NH₄)₂NO₃ | tg | I₄/ a  | 15.874(2) |       |       |       |       |       | PtN₄       |         |         |             |     |
| NHDMe)Ag(  | |       |       |       |       |       |       |       |             |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 16     |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η²-NHCOMe)₂Ag(NH₄)₂NO₃ | tr     | Pm      | 7.143(3) | 8.416(5) | 11.544(6) |       |       |       | PtN₄       |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 2      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η²-NHCOMe)₂Ag(NH₄)₂NO₃ | m     | C₂/c   | 5.345(1) | 23.998(5) | 12.47(4) |       |       |       | PtN₄       |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 8      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η²-MeH)(µ-η³-MeH)Ag(NO₃)₃.H₂O | m     | P2₁/n  | 15.107(3) | 6.971(1) | 24.447(5) |       |       |       | PtN₄       |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 4      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η²-MeH)(µ-η³-MeH)Ag(NO₃)₃.H₂O | tr     | Pm      | 7.520(2) | 12.025(2) | 14.962(3) |       |       |       | PtN₄       |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 2      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η³-NHCOMe)₂Ag(NH₄)₂NO₃ | m     | C₂/c   | 5.345(1) | 23.998(5) | 12.47(4) |       |       |       | PtN₄       |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 8      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η³-NHCOMe)₂Ag(NH₄)₂NO₃ | tr     | Pm      | 7.520(2) | 12.025(2) | 14.962(3) |       |       |       | PtN₄       |         |         |             |     |
| (NO₃)₄H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 2      |       |       |       |       |       |       |             |         |         |             |     |
| cis-[(NH₄)₂Pt(µ-η³-NHCOMe)₂Ag(NH₄)₂NO₃ | tr     | Pm      | 7.520(2) | 12.025(2) | 14.962(3) |       |       |       | PtN₄       |         |         |             |     |
| (NO₄)₂H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 2      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η³-NHCOMe)₂Ag(NH₄)₂NO₃ | m     | C₂/c   | 5.345(1) | 23.998(5) | 12.47(4) |       |       |       | PtN₄       |         |         |             |     |
| (NO₄)₂H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 8      |       |       |       |       |       |       |             |         |         |             |     |
| trans-[(NH₄)₂Pt(µ-η³-NHCOMe)₂Ag(NH₄)₂NO₃ | tr     | Pm      | 7.520(2) | 12.025(2) | 14.962(3) |       |       |       | PtN₄       |         |         |             |     |
| (NO₄)₂H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 2      |       |       |       |       |       |       |             |         |         |             |     |
| cis-[(NH₄)₂Pt(µ-η³-NHCOMe)₂Ag(NH₄)₂NO₃ | tr     | Pm      | 7.520(2) | 12.025(2) | 14.962(3) |       |       |       | PtN₄       |         |         |             |     |
| (NO₄)₂H₂O | |       |       |       |       |       |       |       |             |         |         |             |     |
| (colorless)     |          | 2      |       |       |       |       |       |       |             |         |         |             |     |

Footnotes:
a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. There are four crystallographically independent molecules.
d. Five-membered metallocyclic ring.
e. Six-membered metallocyclic ring.
and \{Pt(acac)\}_2. The repeating unit is shown in Fig. 1(a) and (b) where an inversion center at the midpoint of two Ag(1) atoms is observed. Two of the silver atoms, Ag(1) and Ag(1’), are quadruple bridged by triflates in µ3-0,0” fashion. The \{Ag_2(CF_3SO_3)_4\} moiety has the so called “lantern” type structure. The two external \{Pt(acac)\}_2 units are connected to this \{Ag_2(CF_3SO_3)_4\} moiety through the \{Ag(H_2O)\} units. The repeating units are further connected to each other by the Ag(1)-Pt bond (2.814(1) Å to form the 2-D sheet (Fig. 1c).

Another monoclinic colorless Pt(µ-ox) Ag_2(H_2O)\_2 \[10\] has a stacked 2-D layer structure composed of \(\{Pt(ox)\}_2\)\^2\^- anions and water and a silver(I) atom connected by three types of Ag-O bonds (Table 1). There are two interlayer interactions, one being a Pt to Ag dative bond (2.943(1) Å), and the other a water O(3) to Ag coordination bond (2.502(9) Å).

In triclinic “copper colored” Rb_1.67Pt(ox)\_2.15H_2O \[11\], the planar \{Pt(ox)\}_2 anions stack parallel to the b axis of the crystal. The Pt atoms of non-integral oxidation state Pt(+2.33) form a six-fold distorted chain along the b axis.

Three independent Pt-Pt distances are 2.715(2), 2.832(3) and 3.014(2) Å, with Pt-Pt-Pt angles of 177.93(12) and 174.34(7)°. The oxalate ligands are bidentate -O,O’ and are staggered (46°, 55°, 80°) with respect to the ligands directly above and below them along the chain, while the alternate ligands are eclipsed or staggered (~90°).

There are four independent \(\{Pt(ox)\}_2\)\^3\^- anions based on the assumption of D_{2h} symmetry. The structure contains five independent rubidium atoms, three being seven-, while two are eight- coordinated (Table 1). The neighboring Pt chains are linked by the coordination of the terminal oxygen atoms to the Rb atoms.

In triclinic K_1.6Pt(ox)\_2 × 1.2H_2O complex \[12\] the \(\{Pt(ox)\}_2\)\^2\^- groups are stacked face-to-face along the b axis to form a tetrahedral distorted linear chain. There are two independent Pt-Pt bond distances, Pt(1)-Pt(3) 2.837 and Pt(3)-Pt(2) 2.868 Å and a 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 structure of monoclinic K_2Pt(ox)\_2 × H_2O \[13\] is one-dimensional polymeric.

There are four bis(oxalato)platinate salts of the general formula M Pt(ox)\_x × yH_2O, where M is a bivalent cation: Ni \[14\], Co \[15\], Mg \[16\] or Ca \[17\], x = 0.82 - 1.0 and y = 3.5 - 6.0. Their one-dimensional polymeric structures are similar. Within a platinum chain, oxalate ligands are staggered with respect to the ligands located directly above and below them. The mean Pt-Pt bond distance in these salts is 2.84 Å. The M(II) atoms are located between the planes containing \(\{Pt(ox)\}_2\)\^3\^- anions and are coordinated by water molecules. The Pt(II) atoms are four-coordinated (PtO_4), and the M(II) atoms are six-coordinated (MO_6).

Pale yellow \{Cu(en)\}_0.8Pt(ox)\_2.2H_2O \[18\] has an orthorhombic lattice and a 5-fold platinum sequence along the elongated chain. The mean Pt-Pt bond distance is 2.83(1) Å. Triclinic red brown \{Cu(en)\}_2Pt(ox)\_2 \[19\] contains two crystallographically related planar \(\{Pt(ox)\}_2\)\^3\^- anions and two crystallographically non-equivalent \{Cu(en)\}_2\^2\^- cations. The structure is built up of zig-zag chains of \(\{Pt(ox)\}_2\)\^3\^- anions running in channels formed by the \{Cu(en)\}_2\^2\^- cations. The Pt atoms form a zig-zag chain with alternating Pt...Pt distances of 3.554(1) Å within, the dimers and 3.855(1) Å between the dimers. The Pt...Pt...Pt angle is 140.39°, whereas the line connecting the two Pt atoms of a dimer is tilted by 22° with respect to the normal of the \(\{Pt(ox)\}_2\)\^3\^- plane. The coordination around the Cu(II) atoms is different. Besides its four N neighbors Cu(1) is coordinated to O(8), and to O(8’) (Cu-O 2.55(1) Å) of two adjacent \(\{Pt(ox)\}_2\)\^3\^- anions. Thus the coordination around
Cu(1) is tetragonal bipyramidal (PtN₃O₂). The Cu(2) atom has a somewhat distorted square-planar environment (CuN₄).

The structure of a triclinic \{PtNi\}_n complex [20] contains segregated parallel stacks of \{Pt(ox)\}_3^2 cations, \{Ni(oaoH₂)₂\}_2 cations and neutral \{Ni(oao)₂\}_2 complex units running along an axis, interlinked by a network of strong intermolecular H bridges. All M(II) atoms are tetracoordinated (PtO₄, NiN₄).

The X-ray analysis of triclinic red K₂Pt(memal)₂ × 2H₂O [21] shows that the 2-methylmalonate ligand is in a boat conformation, and their [Pt(memal)₂]²⁻ anionic units stack as a column and chain along the crystallographic a axis, with the Pt...Pt separation of 4.059(2) Å. Hydrogen-bonding interactions between pairs of lattice waters and the O(4) atoms of neighboring anionic units link neighboring “columns” of anionic units in chains that run along the unit cell a,c diagonal. The potassium atom is seven coordinated (KO₇).

The structure of monoclinic pale brown \{PtK₂\}_n complex [22] is built up from the \{Pt(piv)₄\}_2⁻ anion, K⁺ cations and solvate thf molecules, held together by ionic and van der Waals interactions and C-H...O bonds. The Pt(II) atom has a distorted square-planar environment (PtO₄). The nearest environment of the potassium atoms includes six oxygen atoms (KO₆).

Orthorhombic colorless trans-\{(NH₃)₂Pt(µ-meu)₂Ag(NO₃)(H₂O)\} × H₂O [23] has a polymeric structure with PtAg₂ entities linked via O(4) sites of the 1-methyluracilato ligand. The two meu rings in each trinuclear entity are arranged head-to-tail with respect to the Pt-N(3) bonds. They are nearly coplanar with each other (donation 6°). The Pt(II) coordination geometry is close to square-planar (PtN₄). Both silver (I) atoms are coordinated by oxygen (O(4), O(2), of meu H₂O and NO₃⁻). The Pt-Ag bond distances are Pt-Ag(1) 2.896(3) Å and Pt-Ag(2) 2.863(3) Å, and the intermolecular Ag...Ag separation is 3.597 Å.

There are two colorless \{PtAg\}_n complexes, tetragonal cis- and triclinic trans-\{(NH₃)₂Pt(µ-meu)₂Ag(NO₃)(H₂O)\} × nH₂O (n = 4(cis) and 1.5(trans)) [24] for which structural data are available (Table 1). The cations are built up of infinite chains of alternating Pt and Hg atoms bridged by the amidate ligands (Fig. 2). The Pt-Ag bond distances (cis- vs trans-) are 2.897(1) and 2.903(1) Å and 2.925(2) and 2.919(2) Å. The Pt-Ag-Pt angles are 165.7(1)° (cis) and 162.0(1)° (trans). The acetamide moiety is coordinated to Ag via the amide oxygen and to Pt via the deprotonated amide nitrogen. The coordination geometry of Pt(II) is square-planar (PtN₄). The coordination sphere around the Pt atom in the cis- complex is somewhat less crowded than that in the trans- complex as can be seen from the sum of the four Pt-N bond distances, 8.18 vs 8.10 Å.

In polymeric trans- \{(NH₃)₂Pt(µ-pymo)₂Ag(H₂O)\}NO₃ [25] the trans \{(NH₃)₂Pt(pymo)₂\} moiety adopts an anti-conformation. Nevertheless, the \{(H₂O)Ag(pymo)₂\} residues present a syn-conformation that leads to a meander-like global structure. In the polymer the Pt atoms alternate with the Ag atoms. The orientation of the pyrimidine ligands is head-to-tail in the trans-\{(NH₃)₂Pt(pymo)₂\} entities. Silver coordination occurs as expected at the basic N3 donor atom, leading to the polymeric structure. The pyrimidine residues in the \{(H₂O)Ag(pymo)₂\} entities display a head-to-head orientation, which is stabilized by H-bonding interaction with the amino groups bound to Pt of neighboring chain. This results in an alternating head-to-tail orientation of the pyrimidine at the Pt centers, and head-to-head orientation of the pyrimidine residues at the Ag centers, which gives rise to a meander-like overall structure.

The structure of trans-\{(NH₃)₂Pt(meh)(mea)Ag(NO₃)(H₂O)\}²⁺ cation is shown in (Fig. 3) [26]. In the complex cation two purine bases are both coordinated to Pt(II) via the N(7) positions. The Ag(I) atom takes part in a bridging fashion through N(1) and N(3) of 9-methyladenine, leading to a helical \{Ag-N-C-N\}_₈ backbone with 9-methyladenine acting as a tridentate ligand. The Ag...Ag separation
of 5.992(1) Å is shorter than that for Pt...Pt (6.971(1) Å). Methylhypoxantine is not involved in Ag(I) coordination at all and both nucleobases are neutral.

The structure of triclinic colorless trans-\[[\{(\text{NH}_3)_2\text{Pt}(\mu-\eta^2-\text{meh})(\mu-\eta^3-\text{Mea})\text{Ag(NO}_3\text{(H}_2\text{O})\}2\text{Ag}\}. (\text{NO}_3\}3 \times 6\text{H}_2\text{O}\] [27] consists of a purine quartet (two neutral 9-methyladenine (mea) and two anionic 9-methylhypoxantine (meh) units), with four bases cross-linked by two trans- \{(\text{NH}_3)_2\text{Pt}\}^{2+} units and two Ag\(^+\) cations. Individual metalated base quartets, which have dimensions of 14.25(2) Å x 10.36(2) Å (separations between adjacent 9-methyl groups), are bonded through additional Ag\(^+\) cations into an infinite array. The adenine base carries a Pt(II) at N(7) and two Ag(I) at N(1) and N(3). The hypoxantinate carries a Pt(II) at N(7) and one Ag(I) at N(1). Molecular rectangles of the complex cation are roughly parallel (distance ca. 7.0 Å), but slightly shifted, resulting in intermolecular Pt...Pt distances of 7.520(2) Å, which is much shorter than the intramolecular distance of (10.703(3) Å). The Ag...Ag separation is 7.404(3) Å.

Inspection of the data in Table 1 reveals that these complexes crystallize in four crystal systems: tetragonal (x1) < orthorhombic (x5) < monoclinic (x7) < triclinic (x8). The Pt(II) atoms have a distorted square-planar geometry with Pt-O and Pt-N inner coordination spheres. The mean Pt-O bond distance elongates in the order: 1.98 Å (acac) < 2.005 Å (ox) < 2.015 Å (piv) < 2.05 Å (mal). The mean Pt-N bond distances are 2.03 Å (purine bases) < 2.06 Å (NH\(_3\)). There is a variety of bidentate chelated -0,-0\(^-\) ligands which create five-membered metallocyclic rings \{-Pt-OC\(_2\)O\} with the mean O-Pt-O angle of 83°.

There are nine different heterometal atoms (Rb, Mg, Ca and Co (each x1), Cu and Ni (each x2), K (x4) and Ag (x9)) involved in these polymeric platinum complexes, which are mostly one-dimensional. However, from all these heterometal atoms there are only Pt-Ag bond distances which are below 3.0 Å, having a mean value of 2.883 Å (range 2.787(1)–2.943(1) Å). In some of the complexes Pt-Pt bond distances were also found with the mean value of 2.840 Å (range 2.717(3)–2.949(2) Å). The Pt...Pt separations
range from 3.015(3) Å to 10.703(3) Å, and Ag...Ag from 3.597(3) to 7.404(3) Å. However, it must be noted that for some examples the data are not available.

Triclinic Rb$_{0.67}$Pt(ox)$_2 \times 1.5$H$_2$O [11] contains four crystallographically independent molecules within the same crystal differing mostly by degree of distortion and are classical examples of distortion isomerism [29].

### 2.2 Complexes with PtC$_4$ and PtS$_4$ chromophores

There are twenty examples with a PtC$_4$ chromophore and five examples with a PtS$_4$ chromophore, and their crystallographic and structural parameters are listed in Table 2. Monoclinic deep yellow [PtTl$_2$(C$_6$F$_5$)$_2$(C≡CBut)$_2$(Me$_2$CO)$_2$] [30] has a very unusual one-dimensional chain extending along the crystallographic c axis of the lattice, a short section of which is depicted in Fig. 4. Each C$_6$F$_5$ ligand serve as bridge via C atoms to the Pt(II) atom and via one F atom to the Tl(I) atom. In addition the C≡CBut ligand also serve as bridge via C' atom to the Pt(II) and Tl(I) atom. The acetone molecule is terminally coordinated via O atom to the Tl(I) atom. The polymeric complex can be regarded as trinuclear octahedral fragments, trans-trans-trans-{PtTl$_2$(C$_6$F$_5$)$_2$(C≡CBut)$_2$}, linked through alkynyl-thallium interactions. Both Pt-Tl distances within the octahedral unit are 3.135(1) Å, but the Pt...Tl (3.785(1) Å) and Tl...Tl (3.982(1) Å) separations between the units exclude any bonding interaction. Each metal atom is four-coordinate (PtC$_4$, TlF$_2$OC).

There are sixteen polymeric complexes [31-43] in which square-planar {Pt(µ-η$^2$-CN)$_4$}$_2^-$ units are stacked in columns whose axes are occupied by platinum atoms. A wide variety of heterometal atoms are involved in these polymeric (one-dimensional chain) platinum complexes: K (x4), Cu and Yb (each x3), Sn, Sr, Fe, Ni, Zn, Cd, Ag and Eu (each x1). There are also examples which contain KYb [34] and K$_2$M (M = Pb [37] or Sr [38]) with platinum. In general, the CN$^-$ group serves as the bridges {Pt-C-N-M}. The structure of triclinic colorless [(dmf)$_{10}$Yb$_2${Pt(CN)$_4$}]$_2$ [33] is shown in Fig. 5 as an example. It consists of two parallel running zig-zag chains that are inverted with respect to each other. They are generated by {Pt(CN)$_4$}$^{2-}$ ions bridging Yb(III) atoms in a cis-fashion. The chains are linked by a series of {Pt(CN)$_4$}$^{2-}$ units bridging the Yb atoms in a trans-fashion. Each Yb(III) atom is bound to three N (bridging cyanide groups) and five O (dmf) atoms, resulting in slightly distorted square antiprisms. The mean Pt-C(CN) bond distance is 1.99 Å (range 1.96–2.07 Å). The Pt-Pt distances range from 2.85(2) Å [34] to 13.50 Å.

![Figure 4: Section of the polymeric PtTl$_2$(C$_6$F$_5$)$_2$(C≡CBut)$_2$(Me$_2$CO)$_2$ [30].](image4)

![Figure 5: Section of the polymeric [(dmf)$_{10}$Yb$_2$Pt(CN)$_4$]$_2$ [33].](image5)
Table 2: Crystallographic and structural data for heteropolynuclear platinum complexes with PtC₄ and PtS₄ chromophores.

| COMPOUND                                                                 | Cr. sys. | Sp. Grp | Z  | a [Å]   | b [Å]   | c [Å]   | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | M-L-M [°] | L-M-L [°] | Ref  |
|--------------------------------------------------------------------------|----------|---------|----|---------|---------|---------|-------|-------|-------|--------------|---------|---------|-----------|-----------|-----|
| [PtL₂(µ-η²-C₆F₅)₂]₂(µ-C≡CBut)₂(Me₂CO)₂                                      | m        | P2/c    | 4  | 16.197(3)| 23.537(3)| 11.002(1)|       |       |       | PtC₄         | μCσ 2.030(11)| Cₛ²F₂ 2.08(2,3) | μL²F₂.912(8,25) | μC² 2.905(10) | 2.83(2) | 3.785(1) | C, Cl 72.0(3) | 107.8(3) | 30   |
| K₂Pt(µ-η²-CN)₄.Cl₄.2.6H₂O                                               | tg       | P6/mmm  | 2  | 9.866(2) | 5.759(2) |          |       |       |       | PtC₄         | NC 2.06(8)  | 2.07(8) | not given   |           | Pt 2.880(1) | C, C 90.0(-2.6) |           | 31   |
| K₂Pt(µ-η²-CN)₄.Cl₄.2.3H₂O                                               | tr       | P3/m    | 4  | 10.323(14)| 9.285(13)| 11.865(17)|       |       |       | PtC₄         | NC 2.05(9,5) | not given | not given   |           | Pt 2.967(1) | C, C 90.0(3,31) | Pt, Pt 173.2(2) | 32   |
| K₂Pt(µ-η²-CN)₄.3H₂O                                                     | or       | Pbcn    | 4  | 13.426(5)| 11.848(4)| 6.956(2) |       |       |       | PtC₄         | NC 1.982(2) | 1.99(2) | not given   |           | Pt 3.478(1) | C, C 90.0(2,1.9) |           | 32   |
| {[(dnf)₁₀.Yb₂.[Pt(µ-η²-CN)₄]₂}                                          | tr       | P2/1    | 2  | 8.825(1) | 10.546(2)| 99.10(1) |       |       |       | PtC₄         | NC 1.99(2,3) | 2.03(4,3) | dmfO 2.33(3,3) | CN 2.40(4,6) | C, C 88.3(4) | C, C 90.0(12,16) | 177.7(12,10) | 34   |
| {[(NH₄)(dmf)₄.Yb.[Pt(µ-η²-CN)₄]₂}                                        | tr       | P2/1    | 2  | 8.918(1) | 93.27(2) | 98.59(1) |       |       |       | PtC₄         | NC 1.99(6,14)| 172.6(3) | not given   |           | O, O 72.2-152.3(3) | N,N 78.2(10,2.1) | 119.9-141.8(1) | 175.2(9) | 34   |
| {K(dnf)₇.Yb.2.[Pt(µ-η²-CN)₄]₂}                                           | m        | P2/1    | 4  | 9.032(1)| 29.062(1)| 94.51(1) |       |       |       | PtC₄         | NC 1.94(3,1) | 2.03(4,3) | dmfO 2.33(3,3) | CN 2.40(4,6) | C, C 90.0(12,16) | 177.7(12,10) | 34   |
| {K(dnf)₇.Yb.2.[Pt(µ-η²-CN)₄]₂}                                           | tr       | P2/1    | 2  | 8.825(1) | 10.546(2)| 99.10(1) |       |       |       | PtC₄         | NC 1.99(2,3) | 2.03(4,3) | dmfO 2.33(3,3) | CN 2.40(4,6) | C, C 90.0(12,16) | 177.7(12,10) | 34   |
| [Pt(CN)₂(µ-η²-CN)₂.Ag(η⁴-cyclam)]                                         | m        | P2/n    | 2  | 10.253(18)| 9.263(1) | 95.479(7)|       |       |       | PtC₄         | NC 1.99(1) | μNC 1.98(1) | η⁴N 2.020(8,10) | μC² 2.529(9) | C, C 86.6(4) | C, C 90.0(3,4,3) | 180.0 | 36   |
| COMPOUND | Cryst. | Sp. Grp | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | M-L-M [°] | Ref |
|----------|--------|---------|-------|-------|-------|-------|-------|-------|-------------|--------|--------|-----------|-----|
| \{K₂Pb[Pt(μ-η²-CN)₄]₂.6H₂O\} (pale yellow) | m | P₂₁ | 6.487(1) | 17.928(3) | 9.316(2) | 107.76(3) | | | PtC₄ | NC 2.00(2,4) | 3.298(1) | 0.0(2,2) | 37 |
| \{K₂Sr[Pt(μ-η²-CN)₄]₂.6H₂O\} | m | P₂₁ | 9.373 | 17.957 | 6.653 | | | | PtC₄ | SrO₄N₂ | µNC 1.992(3) | 1.993(3) | F,101.08(11) | 38 |
| \{Cu(η²-bpy).Pt(µ-η²-CN₄)₂.2H₂O\} (blue) | tg | P₄₁/mmc | 7.613(2) | 13.501(2) | | | | | PtC₄ | CuN₄ | µNC 1.96(2) | 13.50 | C, C 90.0(1,5) | 40 |
| \{(NH₃)₂MPt(CN)₄.2C₆H₆\} (sky blue) | tg | P₄₁ | 7.60(18) | | | | | | | | Fe 5.243(2) | C, C 90.0(3,3,6) | 41 |
| \{Pt(S₂CNEt₂)₂.Cu₂Cl₂\} (yellow) | | I₄₁/a | 15.855(2) | 15.037(3) | | | | | | | | |
| \{Pt(µ-S₂CNEt₂)₆.Ag₂\}(ClO₄)₂ (orange yellow) | or | Pbcn | 17.166(2) | 11.241(6) | | | | | | | | |
| \{Pt(S₂C₂O₂)₂Mn.(H₂O)₃\}₄.5H₂O (black) | m | P₂₁/c | 11.772(4) | 20.806(11) | 103.52(4) | | | | | | | | 46 |

Continued Table 2: Crystallographic and structural data for heteropolynuclear platinum complexes with PtC₄ and PtS₄ chromophores.

| COMPOUND | Cryst. | Sp. Grp | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | M-L-M [°] | Ref |
|----------|--------|---------|-------|-------|-------|-------|-------|-------|-------------|--------|--------|-----------|-----|
| \{K₂Pb[Pt(μ-η²-CN)₄]₂.6H₂O\} (pale yellow) | m | P₂₁ | 6.487(1) | 17.928(3) | 9.316(2) | 107.76(3) | | | PtC₄ | NC 2.00(2,4) | 3.298(1) | 0.0(2,2) | 37 |
| \{K₂Sr[Pt(μ-η²-CN)₄]₂.6H₂O\} | m | P₂₁ | 9.373 | 17.957 | 6.653 | | | | | SrO₄N₂ | µNC 1.992(3) | 1.993(3) | F,101.08(11) | 38 |
| \{Cu(η²-bpy).Pt(µ-η²-CN₄)₂.2H₂O\} (blue) | tg | P₄₁/mmc | 7.613(2) | 13.501(2) | | | | | | | | |
| \{(NH₃)₂MPt(CN)₄.2C₆H₆\} (sky blue) | tg | P₄₁ | 7.60(18) | | | | | | | | | |
| \{Pt(S₂CNEt₂)₂.Cu₂Cl₂\} (yellow) | | I₄₁/a | 15.855(2) | 15.037(3) | | | | | | | | |
| \{Pt(µ-S₂CNEt₂)₆.Ag₂\}(ClO₄)₂ (orange yellow) | or | Pbcn | 17.166(2) | 11.241(6) | | | | | | | | |
| \{Pt(S₂C₂O₂)₂Mn.(H₂O)₃\}₄.5H₂O (black) | m | P₂₁/c | 11.772(4) | 20.806(11) | 103.52(4) | | | | | | | | 46 |
Table 2: Crystallographic and structural data for heteropolynuclear platinum complexes with PtC4 and PtS4 chromophores.a.

| COMPOUND     | Cr. sys. | Sp.Grp | Z  | a [Å] | b [Å] | c [Å] | α  [o] | β  [o] | γ  [o] | Chromo- | M-L  | M-M [Å] | L-M-M [°] | Ref   |
|--------------|----------|--------|----|-------|-------|-------|--------|--------|--------|----------|------|---------|-----------|-------|
| (K[db18C6])_2 | tr        | Pī     | 1  | 11.819(3) | 99.72(3) | 11.116(1) | 93.479(9) | 82.77(3) | 106.21(2) | PtS4     | 5.2436(6) | 5.087(1) | Cu(40)   | 48    |
| [Pt(SCN)]_4   | P2_/n    |        | 2  | 15.856(1) |        |       |        |        |        | KO N    | 0.7872(2-2.887) | µH2O 2.807 | 0 180  |
| (H2O)         |          |        |    |        |       |       |        |        |        | KO N    | 0.7872(2-2.887) | µH2O 2.807 | 0 180  |

Footnotes:
a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. M = Ni, Cu, Zn or Cd
d. Four-membered metallacyclic ring.

[40]. The Pt-M distances are: 5.087(1) Å (M = Cu [40]), 5.2436(6) Å (M = Fe [41]) and 5.491(1) Å (M = Pb [37]). It must be noted that in most examples the specific data are unavailable.

In two tetragonal yellow Pt(S2CNEt2)CuX2 (X = Cl or Br) [44] examples a helical chain of {CuX}_n extends around a 4_1 axis, and each {Pt(S2CNEt2)}_2 group links two of the helical chains with its four S atoms. Each Cu(I) atom is surrounded by two S and two halogen atoms and has a slightly distorted tetrahedral geometry.

The crystal of orthorhombic orange yellow {PtAg}_2 complex [45] is an alternate pile of extended two-dimensional lattices of {Pt(S2CNEt2)Ag}_n cations and anionic layers containing ClO_4-. The {Pt(S2CNEt2)Ag}_n un, with two extra Pt(S2CNEt2) groups and two extra Ag atoms (all labeled with an X) to show the connections between neighboring units, is shown in Fig. 6. It has C_2 symmetry, with the Pt(1)-Ag(1) bond distance of 2.932(2) Å and the Ag(1)-Pt(1)-Ag(1°) bond angle of 166.8(1)°. The Pt(2) and Ag(1) are separated by 3.045(2) Å, and the Pt(2)-S(3)-Ag(1) angle is 78.2(2)°. Each Pt(II) atom is surrounded by four S atoms in a square-planar geometry. The Ag(I) atom is two coordinate (AgS2).

The structure of monoclinic black {Pt(S2C2O2)2Mn(H2O)}_2 × 4.5H2O [46] consists of extended zig-zag chains {...Pt(S2C2O2)2Mn(H2O)(O2C2S2)Pt...} stacking along and cis-crossing glide plane c. Each layer of stacked chains is separated from the next one by intervening water molecules. The Pt(II) atom is planar tetracoordinated to the sulfur atoms of two dithiooxalate groups. The Mn(II) atom is heptacoordinated to oxygen atoms located at the vertices of a pentagonal bipyramid. Four of these, O(1), O(2), O(3), O(4) belong to two dithiooxalate groups and the others, O_w(1), O_w(2), O_w(3), are from water molecules. Within the chains O atoms [except O_w(1) and O_w(2)] form flat ribbons quasi-perpendicular to glide planes. These ribbons are nearly parallel to crystallographic plane (100).

A structural analysis of triclinic orange [PtK]n complex [47] shows the complex displays a quasi-one-dimensional infinite chain of two {K(db18C6)}+ cations and a [Pt(SCN)]_3 anion, bridged by K...π interactions between adjacent {K(db18C6)}+ units. The principal interactions of the K+ cation involve the six oxygen atoms of the crown and one N atom from the SCN- group. Each Pt(II) atom is in a square-planar environment (PtS2).

The structure of monoclinic orange [(K[18C6])_2[Pt(SCN)]_2(H2O)]_n [48] is shown in Fig. 7. It displays a one-dimensional infinite chain of two (K18C6)+ cations and a (PtSCN)_3 anion bridged alternately by N and O atoms as described below. The Pt(II) atom is located on the two fold axis and is coordinated by four S atoms from four SCN groups, and has a square-planar configuration. The K(1) atom lies almost symmetrically within the crown ether, and is also coordinated by one N atom from the SCN group of the Pt moiety (K-N, 2.837 Å). The two K(1) complex cations share an oxygen atom of a water molecule (K-O, 2.807 Å) which serves as a bridge, with K-O-K angle of 180°, to complete the one-dimensional infinite chain structure.

Inspection of the data in Table 2 reveals that the complexes crystallize in four crystal systems: orthorhombic (x2) < triclinic (x6) < tetragonal (x7) < monoclinic (x8). Each Pt(II) atom has a square-planar arrangement with different degrees of distortion. The sums of all four Pt-L bond distances are 7.87 Å for PtC, and 9.36 Å for PtS2. The PtC4 are less crowded than the PtC4 by virtue of the covalent radii, S (1.02 Å) vs C (0.77 Å). The mean Pt-C vs Pt-S bond distances are 1.97 vs 2.31 Å.
2.3 Complexes with heterogenous chromophores

Crystallographic and structural data for heteropolynuclear platinum complexes with heterogenous coordination spheres about platinum are gathered in Table 3. Their structures are all complex. The X-ray analysis of monoclinic orange KPt(mtso)Cl$_3$ [49] shows that there are two complex {Pt(mtso)Cl$_3$}$^-$ anions differing mostly by degree of distortion. Each Pt(II) atom has a square-planar configuration (PtCl$_3$S). In the crystal structure the potassium atoms differ from each other, with K(1) is surrounded by four chlorine atoms and one oxygen atom and K(2) by six chlorine atoms and one oxygen atom. The mean Pt-Cl bond distance located trans to the S atom is 2.322 Å, which is about 0.021 Å longer than the remaining Pt-Cl bond distances located cis to the S atom (2.301 Å). This difference is caused by the strong trans effect of the sulfoxide ligand.

The structure of triclinic red K$_2$Pt(ox)Cl$_2$.H$_2$O [21] is that of a zig-zag chain. The Pt(II) atom has a square-planar geometry (PtO$_2$Cl$_2$). The chlorine is positioned above the oxalate carbonyl carbon of the adjacent complex, resulting in an electro statistically favored conformation. The Pt...Pt separations are 3.799(2) Å in the same unit cell and 3.815(2) Å in adjacent unit cells. The potassium atoms, K(1) and K(2) are eight- and seven- coordinated, respectively.

The structure of hexagonal yellow {PtAg$_2$}$_n$ complex [50] contains well separated [{((phpy)$_2$Pt$_2$Ag(Me$_2$CO))}$^+$ cations and ClO$_4^-$ anions. The complex cations form
Table 3: Crystallographic and structural data for heteropolynuclear platinum complexes with heterogeneous coordination spheres about Pt∗.

| COMPOUND | Cr. sys. | Sp.Grp | Z | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | L-M-L [°] | Ref |
|----------|----------|--------|---|-------|-------|-------|-------|-------|-------|--------------|--------|--------|-----------|-----|
| Kp(mtsO)Cl3 (orange) | m | P21 | 4 | 15.093(3) | 12.060(3) | 7.499(2) | 101.39(2) | PtCl3S | µCl∗ 2.30(4,10) | 2.322(5,2) | S 2.202(4) | not given | 49 |
| KPt(ox)Cl2.H2O (red) | tr | Pī | 2 | 7.136(2) | 7.308(2) | 10.130(4) | 86.75(3) | 74.58(3) | PtO2Cl2 | O 2.03(1,1) | Cl 2.294(4,4) | not given | 21 |
| \[(\eta^{2}-phasis)Pt\]2\{(\η^{2}-phen)Pt\}2.Ag(Me2CO).ClO4 (yellow) | hx | P6b | 6 | 14.8050(6) | | | | | | | | | |
| \[(\eta^{2}-phil)Pt\]2\{(\η^{2}-mceu)\}.Cs(H2O)2.H2O (colorless) | m | P21/n | 4 | 7.167(1) | 12.900(3) | 18.697(4) | 98.30(3) | 86.61(3) | 15.970(5) | | | CsO I2 | Cs 7.005(2) | 7.167(1) | 3.962(2,26) | 177.46(2) | 177.4(3) | I,I 177.46(2) | N,N 177.4(3) | I,I 177.46(2) | N,N 177.4(3) | 51 |
| \[(NBu4)Pt(C6Cl5)2.\{(µ-Cl)2Ag\} (yellow) | m | C2/c | 4 | 19.300(3) | 26.523(4) | 8.450(2) | 103.53(2) | PtC2Cl2 | C 2.08(2) | µCl 2.324(3) | 2.477(5) | 3.010(8) | Ag 3.203(1) | 3.778(6) | Ag 3.689(6) | RP 177.2(1) | C.C 175.8(8) | 52 |
| Pd(µ-Cl)Pt.\{(µ-η^{2}-C≡CH)\}.Ag(OClO3) (pale yellow) | rh | R3c | 18 | 21.200(4) | | | | | | | | | | |
| [Pt(µSCH2CH2PPh2)2.Ag(NO3)] (colorless) | or | Pbn | 4 | 14.814 | 10.926 | 12.298 | | | | | | | | | | | | |
| KPd(µ-acac)Cl (red) | m | C2/c | 4 | 26.84 | 13.72 | 7.81 | 104.8 | PtO2ClI | O 2.020(14,52) | 2.106(17) | µCl 2.276(5) | not given | 0,0 94.9(6) | 0,0 94.9(6) | 0,0 94.9(6) | 0,0 94.9(6) | 0,0 94.9(6) | 57 |
a helical chain consisting of an alternating stack of \{Pt(phpy)\_2\} and \{Ag(Me\_2CO)\} units connected by Pt → Ag dative bonds (ave 2.772 Å). Since the helical chain has a crystallographic 6\_1 axis and the two sets of platinum and silver units are arranged asymmetrically, one cycle of the helix is comprised of Pt\_12Ag\_12. The helix is about 23 Å in diameter and 41.608 Å in pitch. The grooves of the helices are mutually occupied by adjacent helices. The Pt-Ag-Pt angles of 115.62(3) and 132.76(4)° are somewhat bigger than the Ag-Pt-Ag bond angles with the values of 113.89(3) and 129.51(3)°.

In polymeric monoclinic colorless \[(\text{NH}_3)(\text{I})\text{Pt}(\mu-\text{I})\text{(}\mu-\text{meu})_2\text{Cs(H}_2\text{O})_2\times2\text{H}_2\text{O}\]\([51]\) the Cs(I) atoms bridge the complex ions via water molecules [O\_w(2) and O\_w(4)], as well as through iodine atoms of two anions. The polymeric network of the complex can be dissected into two interconnected chains running along the y and x axes, respectively. In the first one Cs(I) atoms are arranged in a zig-zag fashion (Cs...Cs distances 7.005(2) Å). When viewed along the x axis the Cs(I) atoms are arranged in a collinear fashion, bridging pairs of Pt(II) containing anions (Cs...Cs distances 7.167(1) Å). Each Pt(II) atom

### Table 3: Crystallographic and structural data for heteropolynuclear platinum complexes with heterogeneous coordination spheres about Pt\_+.

| COMPOUND (colour) | Cr. sys. | Sp. Grp. | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | Chromophore | M-L [Å] | M-M [Å] | M-L-M [°] | L-M-L [°] | Ref |
|-------------------|----------|----------|-------|-------|-------|-------|-------|-------|-------------|-------|-------|-----------|-----------|-----|
| (C\_5Cl\_5)PPh\_3Pt. (µ-Cl)\_2Ag | or | Pna\_2\_1 | 10.327(3) | 18.094(6) | 18.451(5) | | | | PtCl\_2CP | | | | | |
| 1.5CH\_3Cl \_2 (yellow) (at 100(l) K) | 4 | | 8.4009(9) | 12.790(2) | 10.467(2) | | | | Pt\_\(n\)O\_2C\_2.\_NBr | | | | | |
| (CH\_3)\_2Pt(µ-Himpa). (µ-Br)\_2Ag | or | Pna\_2\_1 | 13.78(2) | 14.523(4) | 13.38(2) | 118.33(5) | | | Pt\_\(n\)O\_2C\_2.\_NBr | | | | | |
| (µ-Br)Ag | 4 | | 9.98(5) | 5.84(5) | | | | | K\_2Pt(CN)\_5.3H\_2O (red) | | | | | |

Footnotes:

a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

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

c. Five-membered metallocyclic ring.

d. Three-membered metallocyclic ring.
has a square-planar environment (PtN$_2$I$_2$), and the Cs(I) pseudo-octahedral (CsO$_4$I$_2$).

Monoclinic [PtAg]$_n$ complex [52] contains well separated [NBu$_4$]$^+$ cations and [Pt(C$_6$Cl$_5$)$_2$(µ-Cl)$_2$Ag]$^-$ anions. The chain of complex anions consists of planar {Pt(C$_6$Cl$_5$)$_2$Cl$_2$} units linked by Ag(I) atoms in which there are two types of Ag-Cl bond, those which result in Pt(µ-Cl)Ag links and those in which ortho-Cl atoms of C$_6$Cl$_5$ units make close approaches (3.01 nd 3.09 Å) to Ag(I) atoms. The Pt...Ag separation is 3.203(1) Å. Each Pt(II) atom has a square-planar geometry (PtC$_2$Cl$_2$), and the Ag(I) atom is two coordinate (AgCl$_2$).

The structure of triclinic colorless [(PMe$_2$Ph)$_2$Pt(C≡CBut)$_2$Cu$_2$Cl$_2$]$_n$ [53] is shown in Fig. 8. There are two crystallographically independent {Pt(C≡CBut)$_2$(PMe$_2$Ph)$_2$} units in the unit cell, linked to Cu$_2$Cl$_2$ moieties through the alkyne ligands to form a linear polymer. Each Pt(II) atom has a trans-square-planar (PtC$_2$P$_2$) arrangement. Each Cu(I) atom is η$^2$-coordinated to an alkyne group with slightly shorter distances to the β-carbon than to the α-carbon atoms of the alkyne groups (α-distances: Cu(1)-C(9) 2.044(9) Å; Cu(2)-C(23) 2.035(9) Å; β-distances: Cu(1)-C(10) 1.988(9) Å, Cu(2)-C(24) 1.986(9) Å). The copper atoms are linked through double chloro bridges to each other, linking the whole system into a linear chain.

In a linear polymer of [(PMe$_2$Ph)$_2$Pt(C=CH)$_2$Ag(OClO$_3$)]$_n$ [54] each Pt(II) atom has a trans-square-planar arrangement (PtC$_2$P$_2$). The Ag(I) atom is η$^2$-coordinated to each of the two alkyne ligands on the same face of each Pt coordination plane, forming a zigzag chain with a perchlorate anion in each cavity along the chain. In addition to the coordinated Ag-O (2.651(1) Å), there are number of ClO$_4^-$-to-chain contacts which might help to stabilize this arrangement. The Pt...Ag separations are 3.689(6) and 3.778(6) Å.

The X-ray diffraction study of rhombohedral light brown [Pd(µ-Cl)$_n$Pt(µ-C(PPh$_2$)$_2$)$_n$] [55] reveals an infinite chain structure of alternating Pd and Pt units (Fig. 9). The asymmetric unit of the crystal contains one {PdCl$_2$Pt(P(PPh$_2$)$_2$)$_2$} fragment with subsequent units in the infinite chain related by the diagonal glide in which the Pd, Pt, and carbene carbons lie. The coordination units about the metal atoms are coplanar as are the adjacent units of the chain. The Pd(0) is three- (PdCl$_2$C) and the Pt(II) is four (PtCl$_2$P$_2$) coordinate.

Figure 8: Structure of [(PMe$_2$Ph)$_2$Pt(C≡CBut)$_2$Cu$_2$Cl$_2$]$_n$ [53].

Figure 9: Structure of [(PMe$_2$Ph)$_2$Pt(C≡CBut)$_2$Cu$_2$Cl$_2$]$_n$ [53].

In monoclinic red [PtK]$_n$ complex [57] the {Pt(acac)$_2$Cl} anions are linked via electrostatic inter-discrete pseudo-polymeric chains parallel to the crystallographic b axis. Each unit cell contains two such chains separated by van der Waals interactions. The Pt(II) atom has a square-planar geometry (PtO$_2$CCl). The crystallographically non-equivalent linked K$^+$ cations are each six-coordinated; K(1) is coordinated by three pairs of oxygen atoms at distances of 2.72, 2.74 and 2.94 Å, while K(2) is coordinated by a pair of oxygen atoms (2.85 Å) and by two pairs of chlorine atoms at 3.25 and 3.26 Å.

In orthorhombic yellow [(C$_6$Cl$_5$)(PPh$_3$)Pt(µ-Cl)$_2$Ag] × 1.5 CH$_2$Cl$_2$ [58] each of the repeated units of the polymer is formed by interaction of the square-planar trans-Pt(Cl)$_2$(C$_6$Cl$_5$)(PPh$_3$)$_2$ and the Ag$^+$ cation through a Pt-Ag bond (2.855(2) Å), which is supported by a bridging Pt(µ-Cl)$_2$Ag (Ag(1)-Cl(2), 2.556(6) Å and Pt-Cl(2)-Ag(1), 71.6(2)°). The other chlorine atom bonded to the Pt centre Cl(1) acts as a bridge between the Pt and Ag(1A) of a neighboring unit(Ag(1A)-Cl(1), 2.458(5/Å). However, the Ag(A-µCl(1)-Pt(1) angle is 100.7(2)° and the Ag(1A)...Pt(1) separation is 3.679(2) Å.

The structure of orthorhombic colorless [Pt(µ-SCH$_2$CH$_2$Ph)$_2$]$_n$ [56] consists of infinite chains running along the c axis. Each silver(I) atom is coordinated almost linearly to two sulfur atoms belonging to the square-planar coordination spheres of two different platinum(II) atoms (PtS$_2$P$_2$).
In orthorhombic yellow \([\text{Pt(CH}_3\text{)}_2(\mu-\text{Himpa})(\mu-\text{Br})\text{Ag}]_n\) [59] a pseudo-octahedral coordination about the Pt(IV) atom is built up by a tridentate Himpa ligand through N, and phosphonates O atoms trans to methyl group and through carboxylate O atom trans to bromine. The bromine ligand, as well as being bonded to Pt(IV), is also bonded to Ag(1) (Ag-Br, 2.810(2) Å) with a Pt-Br-Ag bond angle of 111.5(1)°. A distorted tetrahedral stereochemistry about silver is completed by three oxygen atoms from different Himpa ligands, a carboxylate oxygen which is not bonded to platinum, a phosphate oxygen which is not protonated and also not bonded to Pt, and a phosphate oxygen which is bonded to \([\text{Pt}(\text{AgO}_3\text{Br})]\). The angles about the Ag(I) atom range from 85.5(1) to 139.5(3)°. The result is a network structure which extends throughout the unit cell in two dimensions.

A view of the extended network of monoclinic white \([\text{PtAg}]_n\) [59] is shown in Fig. 10. There are two complex anions \([\text{Pt}((\mu_3-\text{Br})(\mu-\text{Himpa})(\text{CH}_3)_2)]^-\) and \([\text{Pt}((\mu_3-\text{Br})(\mu-\text{impa})(\text{CH}_3)_2)]^-\) which are isostructural. These anions are held together in a ribbon structure by three independent silver(I) atoms which have quite different environments. While Ag(1) and Ag(2) are each in a distorted trigonal bipyramidal environment, \((\text{AgO}_3\text{Br})\), the Ag(3) atom has a distorted square-pyramidal environment \((\text{AgO}_2\text{Br})\). There are also relatively close contacts (3.2–3.3 Å) between pairs of silver atoms, Ag(1)-Ag(3), Ag(2)-Ag(3) and Ag(2)-Ag(2'). The Ag(1) and Ag(3) are bridged by two carboxylate groups \((\text{Ag(1)}-\text{O(51)}-\text{C(51)}-\text{O(521)}-\text{Ag(3)})\) and \((\text{Ag(1)}-\text{O(522)}-\text{C(52)}-\text{O(512)}-\text{Ag(3)})\), and one phosphate group \((\text{Ag(1)}-\text{O(121')-P(1)}\text{O(111')-Ag(3)})\). The planes of the coordinated carboxylate groups are at an angle of approximately 90°. Each bromine atom bridges between a platinum atom and two silver atoms, Br(1) is bonded to Pt(1), Ag(1) and Ag(3') and Br(2) to Pt(2), Ag(2) and Ag(3)). Each Pt(IV) atom has a pseudo-octahedral environment \((\text{PtO}_2\text{C}_2\text{NBr})\). The Pt(1)-N(31) 2.04(1) Å and Pt(2)-N(32) 2.06(1) Å bond lengths trans to bromine are shorter than the Pt-N bond lengths trans to a methyl group in yellow \([\text{PtAg}]_n\) [59], with the values of 2.18(2) and 2.20(2) Å, respectively. The mean O-Pt-N “bite” angle in the white complex of 85.0° is somewhat more open than the respective angle found in the yellow complex, with the mean value of 82.6°. This can be related to the much stronger trans effect of methyl versus bromine.

The X-ray analysis of tetragonal red polymeric K\(\text{Pt(CN)}_3\cdot3\text{H}_2\text{O}\) complex [60] shows two different platinum atoms, Pt(II) and Pt(IV). The anion chain consists of planar \([\text{Pt(CN)}]_3\) and octahedral \([\text{Pt(CN)}]_6\) units linked by cyanide groups with mean Pt(II)-Pt(IV) bond distance of 2.92 Å. Unfortunately data for the K(I) atom is not available, but one can expect that the cations are also involved in this polymeric chain.

Inspection in data in Table 3 reveals that there are fourteen heteropolymeric platinum complexes which crystallize in several crystal systems: hexagonal, rhombohedral, and tetragonal (each x1) < triclinic (x2) < orthorhombic (x3) < monoclinic (x6). Eleven complexes contain platinum in an oxidation state +2, two contain platinum in oxidation state +4 and one contains mixed-valence +2 and +4. Each Pt(II) atom is four- (square-planar) and each Pt(IV) atom is hexa- coordinated. There are five heterometal atoms Ag (x7), K (x4), Cs, Cu and Pd (each x1), which are involved in these polymeric platinum complexes.

### 3 Conclusions

This review has classified and analyzed over sixty heteropolynuclear platinum complexes. There is only one example which contains a K(I) atom with mixed-valence platinum atoms, Pt(II) and Pt(IV) [60], and two examples in which both Pt(IV) and Ag(I) are found. In all the
remaining examples the platinum is in +2 oxidation state. Each Pt(II) atom has a square-planar environment with different degrees of distortion. There is wide variability of the inner coordination sphere about the Pt(II) atoms: PtO₄ (x14), PtN₄ (x8), PtC₄ (x20), PtS₄ (x5), PtCl₂S, PtO₂Cl₂, PtN₂C₂, PtC₂Cl₂, PtC₂P₂ (x3), PtS₂P₂, PtO₂Cl and PtCl₂CP. In the mixed-valence complex, Pt(II) is planar (PtC₄) and Pt(IV) is octahedral (PtO₂C₂NBr).

There is an example [(NH₃)₂Pt(NHCOMe)₂Ag(NO₃)] x nH₂O [24] which exists in two isomeric forms, cis- (n = 4) and trans- (n = 1.5). There is wide variety of heterometal atoms involved in the heteropolynuclear platinum complexes. There are non-transition: K (x14), Mg, Ca, Sr, Tl, Sn, Pb, Zn and Cd (each x1); transition: Ag (x16), Cu (x6), Ni (x3), Fe, Rh, and Pd (each x1), and even lanthanide: Yb (x3) and Eu (x1). In spite of the wide variability of the heterometal atoms, there is only “real” Pt-M bond with Ag, ranging from 2.6781(9) Å [50] to 2.943(1) Å [10] (ave 2.855 Å). There are also examples in which the Pt...Ag separation is over 3.0 Å, range from 3.045(2) Å [45] to 3.778(6) Å [54] (ave 3.479 Å). The mean Pt-Pt bond distance is 2.869 Å (range 2.717(3) Å [11] – 2.976(1) Å [32]). In several examples the Pt...Pt separation is over 3.0 Å (3.015(3) Å [11], 13.50 Å [40]).

This review, together with its precursors [1-9], represents the first comprehensive overview of about one thousand and five hundred heterometallic platinum clusters for which structural parameters were available, illustrating a rich diversity in the chemistry of platinum. These clusters crystallize in seven different crystal systems: monoclinic (57.3%) > triclinic (29.5%) > orthorhombic (9.2%) > tetragonal (2.55%) > hexagonal (0.52%) > trigonal (0.46%) > rhombohedral (0.27%) > cubic (0.2%). Space groups P2₁/n and Pī are by far the most prevalent. There are almost sixty clusters [61-116] which contain two crystallographically independent molecules within the same crystal. In PtOs₇(H₂)₃(CO)₁₅ [117] three such molecules are present, in (PPh₃)₄Pt(S)₂Fe(CO)₄ [118] four molecules and in Cl₂Pt(totpp),Fe [119] eight such molecules are present. All these molecules differ mostly by degree of distortion. The coexistence of such molecules is typical of the general class of distortion isomerism [29]. There are also nine derivatives [94,96,120-127] which exist in two isomeric forms. These isomers differing from each other only by degree of distortion are also examples of distortion isomerism.

Analysis of the crystallographic and structural data of almost two thousand monomeric platinum coordination compounds showed [128] that about 10% of these complexes exist as isomers: distortion (65%), cis-trans (30%), mixed isomers (cis-trans plus distortion), and ligand isomerism. Despite the importance of cis-trans geometry in the chemistry of Pt(II) compared to other transition metal systems, within platinum chemistry, distortion isomerism is far more common.

It is hoped that this overview will help to focus attention on the area of platinum chemistry that could be enhanced by further study, and assist in allowing comparative behavior of the platinum atom in the situations which can arise from the wide spread use of platinum.

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**Abbreviations**

- acac: acetylacetonate
- bpe: 1,2-bis(4-pyridyl)ethylene
- bpy: 2,2’-bipyridyl
- Bu: butyl
- Bu': terc-butyl
- C₆Cl₅: pentachlorophenyl
- C₆F₅: pentafluorophenyl
- C₆H₆: benzene
- 18C₆: 18-crown-6
- cyclam: 1,4,8,11-tetraazacyclotetradecane
- db18C₆: dibenzo-18-crown-6
- dmf: dimethylformamide
- en: ethylenediamine
- Et: ethyl
- Himpa: N-(phosphonomethyl)glycinate(2-)
- hx: hexagonal
- impa: N-(phosphonomethyl)glycinate(3-)
- m: monoclinic
- Me: methyl
- Me₂CONH: acetamidate
- mea: 9-methyladenine
- meh: 9-methylhypoxantin
- memal: 2-methylmalonate
- meu: 1-methyluracilate
- mtso: methyl-para-tolyl-sulfoxide
- oao: oxamide oximato
- oaoH₂: oxamide oxime
- or: orthorhombic
- ox: oxalate
- phpy: 2-phenylpyridinate
- piv: pivalate
- PMe₂Ph: dimethylphenylphosphine
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