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Mercury and platinum mixed cluster having a prismatic structure, $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$*

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Abstract

Mixed cluster, $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (**1**) was crystallized in the monoclinic space group *Cc* with $a = 27.2930(1)$, $b = 15.7928(3)$, $c = 24.5154(1)$ Å, $\beta = 102.369(2)°$, $V = 10321.7(3)$ Å^3 and $Z = 4$. Block-diagonal least-squares refinement converged at $R = 0.0481$ and $R_w = 0.0540$. The six platinum atoms define a trigonal prism. The two triangular Pt_3 fragments show a rotational distortion from an eclipsed D_{3h} configuration by *c*. 11°. The mercury atom occupies the pseudocenter of the prism. Each triangular edge is associated with one terminal and two bridging isocyanide groups. From an X-ray photoelectron spectrum, the bonding between Hg and two Pt_3 cores is neutral. The electronic structure was discussed from the EHMO calculation of $[HgPt_6(HNC)_{12}]$. Cluster geometry was also investigated. The cluster has 96 electrons, in good agreement with the valence electron number found by Mingos' consideration for a condensed polyhedron.

Key words: Crystal structures; Mercury complexes; Platinum complexes; Isocyanide complexes; Cluster complexes

Introduction

Since the pioneering work of Chatt and Chini, a large number of triangular clusters of platinum and its related metals have been characterized [2]. The platinum carbonyl clusters are represented by the formula $[Pt_3(\mu_2\text{-}CO)_3(CO)_3]_n^{2-}$ ($n = 2, 3, 4, 5, 6, 10$) [3]. The structure of this series has been confirmed as a distorted D_{3h} stacking arrangement. The existence of the monomer $[Pt_3(CO)_6]^{2-}$ in solution has been inferred from ^{195}Pt NMR studies. These species have 44 valence electrons. Similar triangular complexes of isocyanide are neutral and have 42 valence electrons [4, 5].

Previously we reported the preparation and crystallographic analysis of a seven platinum cluster containing only an isocyanide ligand, which was derived from a distorted trigonal-bipyramidal unit as the main framework, and is a 96-electron cluster [6]. In an attempt to prepare other isocyanide clusters, we have obtained a new mixed-metal cluster, $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (**1**) involving a mercury atom in the center of a trigonal-prismatic platinum core [5]. Recently we reported the preparations of $[Hg_2Pt_6(diphos)_2(RNC)_8]$, $[Hg_2Pt_6(diphos)_3(RNC)_6]$ and $[HgPt_6(dppb)_2(RNC)_8]$ (diphos = $Ph_2P(CH_2)_nPPh_2$, $n = 5$ or 6; dppb = $Ph_2P(CH_2)_4PPh_2$), which contain an Hg or Hg_2 unit in the center of the cage-type Pt_6 core supported by diphosphines [7]. It is of particular interest to investigate the electronic structure of triangular triplatinum cores in comparison with those of anionic or neutral triplatinum complexes of carbonyl and isocyanide. Here we report the X-ray crystallographic analysis and electronic structure of the mixed-metal cluster **1**.

Results and discussion

Description of the crystal structure

The molecular geometry of $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (**1**) is shown in Fig. 1. Bond distances and angles are given in Table 1. The molecule is a mixed-metal cluster derived from one mercury and six platinum atoms. The six platinum atoms define a trigonal prism;

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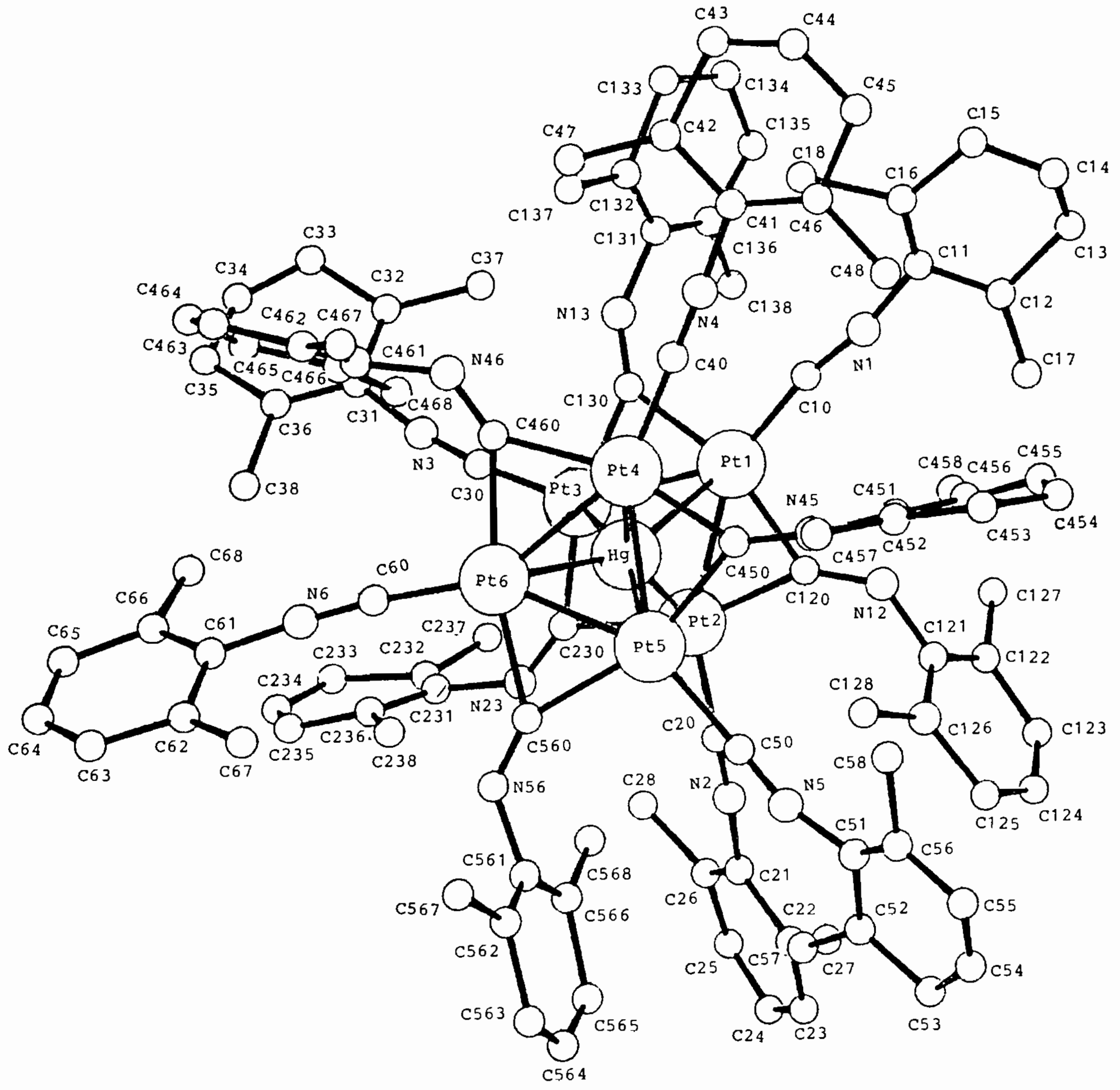


Fig. 1. Structure of $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$.

the edges of the triangles are associated with six bridging and six terminal isocyanide ligands. The mercury atom occupies the pseudocenter of the prism. The molecule shows a small rotational distortion of the two triangular Pt_3 fragments from an eclipsed D_{3h} configuration by *c.* 11° (torsion angles: Pt(1)–Hg–Pt(4)–C(40) = 11.9(19)° and Pt(4)–Hg–Pt(1)–C(10) = 10.9(17)°). The intertriangular Pt–Pt distances occur between the Pt(1)–Pt(4) bond of 4.854(3) Å (the closest distance) and the Pt(3)–Pt(5) bond of 5.938(3)° (the longest distance), suggesting the absence of the direct interaction between platinum triangles. The dihedral angle between two triangles is 7.41(8)°. The carbon atoms of the terminal and bridging isocyanides except the C(10) atom are located at opposite sides of the mercury atom. This is probably responsible for minimizing the steric repulsion of ligands. The Hg atom is nearly equidistant (*c.* 2.51 Å) from each of the two Pt_3 planes. The Hg–Pt distances are between 3.010(3) and 2.900(2) Å, and are longer than the sum (2.79 Å) of each of the covalent radii. They are slightly longer than those (Pt–Hg = 2.859(2)–2.970(2) Å) [8] of the $[Pt_3(\mu_3\text{-}Hg)(\mu_3\text{-}CO)(\mu\text{-dppm})_3]^{2+}$ complex and slightly shorter than those (Pt–Hg = 2.932–3.084 Å) found for $[Hg_2Pt_6(\mu\text{-}CO)_6(PPh\text{-}i\text{-}Pr_2)_6]$ [9]. They are also longer than the Pt–Hg(II) bond length (Pt–Hg = 2.572(1) Å) found for $[(\eta^5\text{-}C_5H_5)WHgPt(PPh_3)_2(C_6Cl_5)]$ [10]. The Pt–Pt distances ranging from 2.664(2) to 2.633(2) Å are comparable with those found in $[Hg_2Pt_6(\mu\text{-}CO)_6(PPh\text{-}i\text{-}Pr_2)_6]$ [9], $Pt_3(\mu\text{-}t\text{-}BuNC)_3(t\text{-}BuNC)_3$ [4a], and $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$ [6]. The average distances for Pt–C(terminal) and Pt–C(bridged) bonds are 1.91(5)

TABLE 1. Bond distances and angles of [$HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}$]

Bond distances (Å)			
Hg–Pt(1)	2.900(2)	Pt(2)–C(120)	2.027(55)
Hg–Pt(2)	2.930(3)	Pt(2)–C(230)	2.146(38)
Hg–Pt(3)	3.010(3)	Pt(3)–C(30)	1.838(42)
Hg–Pt(4)	2.924(3)	Pt(3)–C(130)	2.016(40)
Hg–Pt(5)	2.972(3)	Pt(3)–C(230)	2 006(37)
Hg–Pt(6)	2 919(2)	Pt(4)–C(40)	1 883(51)
Pt(1)–Pt(2)	2 636(2)	Pt(4)–C(450)	2 025(51)
Pt(1)–Pt(3)	2 642(3)	Pt(4)–C(460)	2.185(62)
Pt(1)–Pt(4)	4.854(3)	Pt(5)–C(50)	2.077(48)
Pt(1)–Pt(5)	5.474(3)	Pt(5)–C(450)	2.114(49)
Pt(1)–Pt(6)	5.708(2)	Pt(5)–C(560)	2 185(62)
Pt(2)–Pt(3)	2.633(2)	Pt(6)–C(60)	1.865(62)
Pt(2)–Pt(4)	5.757(3)	Pt(6)–C(460)	2.185(44)
Pt(2)–Pt(5)	5.175(3)	Pt(6)–C(560)	2.163(61)
Pt(2)–Pt(6)	5.568(2)	C(10)–N(10)	1.21(6)
Pt(3)–Pt(4)	5.508(3)	C(20)–N(20)	1.06(6)
Pt(3)–Pt(5)	5.938(3)	C(30)–N(30)	1.19(5)
Pt(3)–Pt(6)	5.166(3)	C(40)–N(40)	1.13(8)
Pt(4)–Pt(5)	2.664(2)	C(50)–N(50)	1.11(6)
Pt(4)–Pt(6)	2.639(3)	C(60)–N(60)	1.16(6)
Pt(5)–Pt(6)	2.645(3)	C(120)–N(12)	1.26(7)
Pt(1)–C(10)	1.912(51)	C(130)–N(13)	1.19(5)
Pt(1)–C(120)	2.043(54)	C(230)–N(23)	1.19(5)
Pt(1)–C(130)	2.105(42)	C(450)–N(45)	1.27(7)
Pt(2)–C(20)	1.912(47)	C(460)–N(46)	1.19(6)
		C(560)–N(56)	1 15(7)
Bond angles (°)			
Pt(1)–Hg–Pt(2)	53.77(6)	Pt(1)–C(120)–N(12)	134.6(40)
Pt(1)–Hg–Pt(3)	53 06(6)	Pt(1)–C(120)–Pt(2)	80 7(20)
Pt(2)–Hg–Pt(3)	52.60(6)	Pt(2)–C(120)–N(12)	144.5(42)
Pt(4)–Hg–Pt(5)	53.70(6)	C(120)–N(12)–C(121)	134.6(42)
Pt(4)–Hg–Pt(6)	53.70(6)	Pt(1)–C(130)–N(13)	136.2(33)
Pt(5)–Hg–Pt(6)	53.35(7)	Pt(1)–C(130)–Pt(3)	79.7(15)
Pt(1)–Pt(2)–Pt(3)	60.17(7)	Pt(3)–C(130)–N(13)	143.0(36)
Pt(1)–Pt(3)–Pt(2)	59.98(7)	C(130)–N(13)–C(131)	146.9(42)
Pt(2)–Pt(1)–Pt(3)	59.85(7)	Pt(2)–C(230)–N(23)	148.8(33)
Pt(4)–Pt(5)–Pt(6)	59.62(6)	Pt(3)–C(230)–N(23)	133.8(38)
Pt(4)–Pt(6)–Pt(5)	60.53(7)	C(230)–N(23)–C(231)	133.8(38)
Pt(5)–Pt(4)–Pt(6)	59.84(7)	Pt(4)–C(450)–N(45)	142.8(39)
Pt(1)–C(10)–N(10)	169.2(43)	Pt(4)–C(450)–Pt(5)	80 1(18)
C(10)–N(10)–C(11)	169.6(47)	Pt(5)–C(450)–N(45)	137.2(38)
Pt(2)–C(29)–N(20)	170.9(45)	C(450)–N(45)–C(451)	171.8(38)
C(20)–N(20)–C(21)	166.8(50)	Pt(4)–C(460)–N(46)	141.2(35)
Pt(30)–C(30)–N(30)	170.1(31)	Pt(4)–C(460)–N(46)	141.2(35)
C(30)–N(30)–C(31)	171.3(40)	Pt(6)–C(460)–Pt(6)	75.3(15)
Pt(4)–C(40)–N(40)	167.8(44)	C(460)–N(46)–C(461)	132.9(38)
C(40)–N(40)–C(41)	173.7(49)	Pt(5)–C(560)–N(56)	146.1(51)
Pt(5)–C(50)–N(50)	178.3(42)	Pt(5)–C(560)–Pt(6)	74.9(19)
C(50)–N(50)–C(51)	161.2(53)	Pt(6)–C(560)–N(56)	138.9(51)
Pt(6)–C(60)–N(60)	173.4(38)	C(560)–N(56)–C(561)	133 2(50)
C(60)–N(60)–C(61)	169.6(42)	Pt(2)–C(230)–N(23)	148.8(33)

and 2.10(5) Å, respectively, and closely resemble those found in other platinum isocyanide complexes. There are some asymmetric distances (Pt(1)–C(130) = 2.11(4), Pt(3)–C(130) = 2.02(4), Pt(2)–C(230) = 2.15(4), Pt(3)–C(230) = 2.01, Pt(4)–C(450) = 2.03(5), Pt(5)–C(450) = 2.11(5) Å) in the isocyanide bridges. The mean Pt–C–N and C–N–C bond angles associated with terminal groups are *c.* 172 and 168°, respectively. They deviate slightly from those (av. 175° for Pt–C–N and C–N–C bonds) found in $Pt_3(\mu\text{-t-BuNC})_3(\text{t-BuNC})_3$, due to bulky 2,6-xylyl isocyanide.

The most remarkable bonding mode was found in one of the bridging isocyanide ligands, a C(450)–N(45)–C(451) angle of 171.8(38)°, markedly contrasted with the usual value (*c.* 135°) of C–N–C angles of bridging isocyanide ligands. Since this bonding mode reflected the intermolecular non-bonded distances (3.62 Å of the C(451)...C(48) and 3.78 Å of the C(451)...C(58) bonds) and no energy difference was found between the bent and linear bridging isocyanide structures, the linearity of the bridging isocyanide was probably due to steric or crystal packing effects. Linearity of bridging isocyanide groups (*c.* 175°) has been observed in [$Pd_2Cl_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2(\text{pyridine})_2$] [11] and $Pd_2(C_5HPh_4)_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2$ [12].

The non-bonding close contacts between the two Pt_3 triangles in the molecule are C(18)...C(46) of 3.57(9) Å and C(27)...C(57) of 3.67(8) Å, and the close contacts in each Pt_3 fragment are C(18)...C(136) of 3.60(10) Å and C(58)...C(457) of 3.57(9) Å, smaller than the sum (3.8 Å) of the van der Waals radii of a carbon atom (Table 2). The close intermolecular contacts are C(28)...C(56) (x, $-y$, $\frac{3}{2}+z$) of 3.43(6) Å, C(28)...C(58) (x, $-y$, $\frac{3}{2}+z$) of 3.47(7) Å, C(24)...C(33) (x, $1-y$, $1+z$) of 3.48(9) Å and C(32)...C(467) (x, $-y$, $\frac{3}{2}+z$) of 3.51 Å. These contacts are comparable with the closest contact (3.55(4) Å) in the unit cell of $Pt_3(\mu\text{-t-BuNC})_3(\text{t-BuNC})_3$.

Cluster geometry

There is a general correlation between polyhedron geometry and the number of valence electrons in the skeleton orbitals. The seven-atom clusters are relatively rare and their frameworks appear to adopt a monocapped octahedral, $[Rh_7(CO)_{16}I]^{2-}$ [13] and $Pd_7(CO)_7(PMe_3)_7$ [14], bicapped trigonal-bipyramidal,

TABLE 2. Inter- and intra-molecular non-bonded distances

Intermolecular (<3.8 Å)			
C(18)· ·C(46)	3.57(9)	C(48)···C(451)	3.62(10)
C(18)· C(136)	3.60(10)	C(27)···C(57)	3.67(8)
C(58)· C(457)	3.57(9)	C(68)·· C(468)	3.73(8)
C(18)···C(138)	3.80(10)	C(57)···C(566)	3.73(8)
C(28) · C(238)	3.76(9)	C(58)···C(451)	3.78(7)
Intermolecular (<3.75 Å)			
Pt(2)·· C(55a)	3.70(5)	C(25)···C(33d)	3.60(8)
Pt(6)·· C(33b)	3.70(6)	C(26)· C(58b)	3.68(6)
C(13)· ·C(24c)	3.75(8)	C(28) · C(56b)	3.43(b)
C(13)·· C(25c)	3.75(8)	C(28)···C(58b)	3.47(7)
C(23)···C(468d)	3.54(7)	C(31)···C(467b)	3.69(8)
C(24)·· C(33d)	3.48(9)	C(32)···C(67b)	3.74(9)
C(24)···C(13c)	3.75(8)	C(35)· ·C(67b)	3.74(9)

a: $x+1$, $-y+1$, $z+(\frac{3}{2})$. b: $x+1$, $-y$, $z+(\frac{3}{2})$. c: $-x$, $-y$, $-z+1$. d: x, $y+1$, $z+1$.

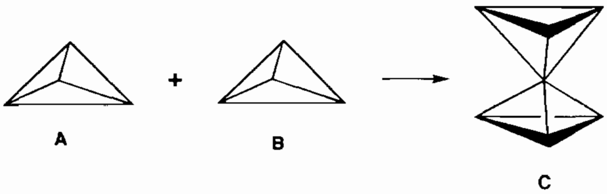
$Au_3CoRu_3(CO)_{12}(PPh_3)$ [15], or a metal cluster arrangement, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$, derived from the bicapped trigonal-bipyramidal geometry [6].

Structures of metal clusters are often described in the terms of a condensed polyhedron based on octahedral, tetrahedral and triangular fragments. Mingos investigated the factors governing the number and type of bonding molecular orbitals generated when two polyhedra condense, and produced a widely applicable generalization for predicting the number of cluster valence molecular orbitals in condensed clusters [16].

On the basis of his investigation, the present cluster is condensed to a geometry C (electron count c) joined through each vertex of the two tetrahedral fragments A (electron count a) and B (electron count b) (Scheme 1). In the condensed cluster C, the number of electron is counted as $a+b-18=c$. The tetrahedral fragments A and B consist of one metal (Hg atom), utilizing nine valence orbitals, and of three metal (Pt atom), utilizing eight. The electron count of A and B by Mingos' generalization is calculated to be 57 electrons ($a=b=56\times3/4+60\times1/4=57$). Thus the preferred electron count of the sandwiched cluster structure is predicted to be 96 electrons ($a+b-18=c$). The electron count shows that **1** is a 96-electron cluster similar to that of the seven platinum cluster, $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$ and is in good agreement with the condensed generalization. The mixed-metal cluster **1** is not an unusual one.

Electronic structure

Two possible structures for electronic configurations of **1** are considered: (i) from the similarity to $[Pt_3(CO)_6]_n^{2-}$, the $[Pt_6(RNC)_{12}]$ fragment has a divalent negative charge and the mercury atom, Hg^{2+} and (ii) mercury and two $[Pt_3(RNC)_6]$ fragments are neutral [17]. In an attempt to examine the electronic structure the X-ray photoelectron spectra were measured. The results are given together with those of the related complexes in Table 3. The binding energy (BE) of **1** is 72.4 eV for the Pt $4f_{7/2}$ core level and 75.4 eV for the Pt $4f_{5/2}$ one, being in good agreement with those of zerovalent $Pt_3(RNC)_6$ complexes. The BE of the Hg $4f_{7/2}$ core was 101.4 eV. For comparison, the BEs of Hg metal and $HgCl_2$ were measured; the former is 101.5 eV and the latter, 101.9 eV. From these results, complex **1** is assumed to have an electronic structure built from neutral Hg and $Pt_3(2,6\text{-}Me_2C_6H_3NC)_6$ fragments.



Scheme 1. Framework of $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (ligands omitted for clarity).

TABLE 3. Binding energies of platinum and mercury (eV)[a,b]

Complex	Pt		Hg
	$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$
$[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$	72.4 (1.9)	75.4 (2.0)	101.4 (1.1)
$Pt_3(2,4,6\text{-}t\text{-}Bu_3C_6H_2NC)_6$	72.2 (2.1)	75.3 (2.1)	
$Pt_3(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_3NC)_6$	72.2 (1.6)	75.3 (1.6)	
$PtCl_2(2,4\text{-}t\text{-}Bu_2\text{-}6\text{-}MeC_6H_3NC)_6$	74.4 (1.3)	77.4 (1 3)	

[a] Values (eV) in parentheses are a peak full widths at the half-maxima. [b] Hg: $4f_{7/2}$ 101.5 (1.2) eV and $HgCl_2$. $4f_{7/2}$ 101.9 (1.7) eV.

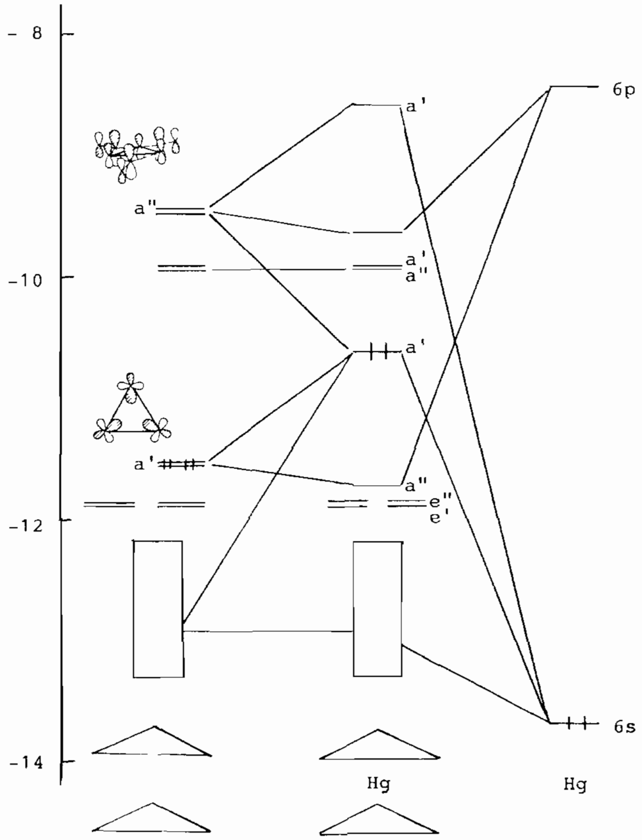


Fig. 2. Molecular orbital of $[HgPt_6(HNC)_{12}]$

In an analysis of the bonding in complex **1** (as D_{3h} symmetry), the strongest interactions are calculated to be unfavorable ones between doubly occupied orbitals on Hg (6s orbital) and Pt (filled orbitals) (Fig. 2). There is a weak interaction of the Hg 6s orbital with the vacant a″ (mostly $6p_z$) orbital on Pt. This interaction slightly stabilizes the repulsive HOMO–HOMO interaction. There also exists weak backbonding from the filled d orbitals on Pt to the empty Hg $6p_z$ orbital. Similar interactions have been observed in the EHMO calculation of $[Hg_2Pt_6(\mu\text{-}CNH)_6(PH_3)_6]$ [7]. This weak interaction between Hg and Pt_3 cores may be deduced by the fact that the thermal reaction of **1** in toluene at reflux undergoes a cleavage of mercury–platinum bonds to give the triangular $Pt_3(2,6\text{-}Me_2C_6H_3NC)_6$ complex.

Experimental

The complex, $[HgPt_6(2,6\text{-}Me_2C_6H_3NC)_{12}]$ (**1**) was prepared according to the literature [5].

X-ray data and structure determination

Dark green crystals of **1** were obtained from a mixture of benzene and n-hexane. X-ray photographic data from Weissenberg photographs showed the crystal to be monoclinic with systematic extinctions (hkl, $h+k=2n$; $h0l$, $l=2n$) consistent with the space group Cc or $C2/c$. Successful solution and refinement of the structure confirmed the former as the correct choice. The crystal with six faces of the form $[(100)(\bar{1}00)(010)(0\bar{1}0)(001)(00\bar{1})]$ was mounted on a Rigaku four-circle diffractometer. Intensities were corrected for Lorentz and polarization effects. Of the total 4567 reflections, 4249 reflections were observed as $F_o > 4\sigma(F_o)$.

TABLE 4. Crystallographic data and data collection

Space group	Cc
Molecular weight	2945.3
a (Å)	27.2930(1)
b (Å)	15.7928(3)
c (Å)	24.5154(1)
β (°)	102.369(2)
V (Å^3)	10321.7(3)
Z	4
D_{calc} (g/cm)	1.89
D_{obs} (g/cm)	1.85
Crystal size (mm)	0.078 × 0.44 × 0.2
Radiation, λ (Å)	graphite monochromated Mo Kα, 0.7107
Scan type	ω–2θ
Collection range	$2 < 2\theta < 45$
Scan rate (°/min)	4
Unique data collection	4565
Data used for structure, $F_o > 4\sigma(F_o)$	4249
No. variables	545
R^a	0.0481
$R_w{}^b$	0.0540

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 5. Positional parameters[a]

Atom	x	y	z
Hg	0(1)	−2558(1)	0(1)
Pt1	−817(1)	−2571(1)	−975(1)
Pt2	−157(1)	−1338(1)	−922(1)
Pt3	74(1)	−2880(1)	−1190(1)
Pt4	−211(1)	−3567(1)	923(1)
Pt5	164(1)	−2028(1)	1189(1)
Pt6	740(1)	−3248(1)	933(1)
N1	−187(1)	−319(2)	−85(2)
N2	16(1)	45(3)	−94(2)
N3	67(1)	−413(2)	−171(1)
N4	−106(1)	−477(2)	90(2)
N5	−5(2)	−19(3)	163(2)
N6	180(1)	−377(2)	92(1)
N12	−124(1)	−82(2)	−82(2)
N13	−69(1)	−430(2)	−150(1)
N23	90(1)	−153(2)	−117(1)
N45	−94(1)	−234(3)	136(2)
N46	39(1)	−519(2)	69(1)
N56	132(2)	−157(3)	130(2)
C10	−145(2)	−303(3)	−91(2)
C11	−232(2)	−352(3)	−78(2)
C12	−267(2)	−285(4)	−82(3)
C13	−320(2)	−314(4)	−78(3)
C14	−324(3)	−375(5)	−57(3)
C15	−291(3)	−442(6)	−52(4)
C16	−240(2)	−424(4)	−58(2)
C17	−260(3)	−196(5)	−101(3)
C18	−195(3)	−493(5)	−49(3)
C20	5(2)	−18(3)	−89(2)
C21	32(1)	123(2)	−114(2)
C22	26(2)	200(3)	−78(2)
C23	40(2)	279(3)	−101(2)
C24	57(2)	283(4)	−148(3)
C25	59(2)	215(4)	−183(2)
C26	50(2)	129(3)	−162(2)
C27	8(2)	194(4)	−25(2)
C28	62(2)	47(3)	−191(2)
C30	48(1)	−363(3)	−147(2)
C31	85(2)	−483(3)	−200(2)
C32	48(2)	−525(3)	−241(2)
C33	72(2)	−600(4)	−264(2)
C34	121(2)	−603(4)	−254(2)
C35	156(2)	−571(4)	−216(2)
C36	133(1)	−505(2)	−189(2)
C37	−8(2)	−497(4)	−254(2)
C38	173(2)	−458(3)	−141(2)
C40	−76(2)	−432(3)	84(2)
C41	−145(2)	−538(3)	90(2)
C42	−132(2)	−622(4)	82(3)
C43	−180(2)	−681(3)	87(2)
C44	−217(3)	−645(5)	96(3)
C45	−230(2)	−564(4)	104(2)
C46	−188(2)	−506(9)	98(2)
C47	−79(3)	−644(5)	74(3)
C48	−201(3)	−413(5)	103(3)
C50	2(2)	−83(3)	147(2)
C51	−24(2)	45(3)	188(2)
C52	−7(2)	121(3)	166(2)
C53	−24(2)	197(3)	193(2)
C54	−50(2)	175(3)	235(2)
C55	−62(2)	108(3)	255(2)
C56	−46(2)	39(3)	231(2)
C57	25(2)	129(4)	122(3)
C58	−65(2)	−47(3)	246(2)
C60	139(2)	−362(3)	92(2)
C61	232(2)	−393(3)	102(2)
C62	261(2)	−365(4)	151(2)

(continued)

TABLE 5 (*continued*)

Atom	x	y	z
C63	313(2)	−386(3)	166(2)
C64	332(2)	−421(3)	125(2)
C65	307(2)	−443(3)	70(2)
C66	254(2)	−428(3)	60(2)
C67	239(2)	−332(4)	197(3)
C68	222(2)	−446(4)	1(2)
C120	−89(2)	−130(3)	−86(2)
C121	−129(2)	8(3)	−75(2)
C122	−105(2)	38(3)	−21(2)
C123	−114(3)	134(5)	−12(3)
C124	−143(2)	171(4)	−60(2)
C125	−163(2)	140(4)	−109(2)
C126	−159(2)	51(3)	−121(2)
C127	−74(2)	−13(3)	24(2)
C128	−184(2)	11(4)	−172(2)
C130	−53(1)	−365(3)	−129(2)
C131	−112(2)	−482(3)	−168(2)
C132	−145(2)	−454(4)	−216(2)
C133	−190(2)	−497(4)	−234(3)
C134	−194(3)	−577(5)	−208(3)
C135	−159(2)	−612(4)	−162(3)
C136	−112(2)	−555(4)	−137(2)
C137	−140(3)	−375(4)	−252(3)
C138	−77(2)	−581(4)	−85(3)
C230	51(1)	−184(2)	−114(1)
C231	135(1)	−186(3)	−125(2)
C232	175(2)	−211(3)	−81(2)
C233	221(2)	−230(3)	−96(2)
C234	223(2)	−237(4)	−148(2)
C235	186(2)	−223(4)	−197(3)
C236	137(2)	−185(3)	−181(2)
C237	170(2)	−201(3)	−26(2)
C238	94(2)	−174(4)	−228(3)
C450	−54(2)	−257(3)	123(2)
C451	−138(2)	−219(4)	156(2)
C452	−133(2)	−235(3)	212(2)
C453	−178(2)	−211(4)	230(2)
C454	−220(3)	−173(5)	189(3)
C455	−220(2)	−177(4)	139(3)
C456	−180(2)	−185(4)	111(3)
C457	−90(3)	−269(5)	248(3)
C458	−178(2)	−179(4)	55(2)
C460	34(2)	−446(3)	80(2)
C461	80(2)	−567(3)	60(2)
C462	102(2)	−616(3)	107(2)
C463	138(2)	−671(4)	95(2)
C464	149(2)	−675(4)	43(3)
C465	68(2)	−498(3)	−34(2)
C466	90(2)	−559(3)	12(2)
C467	83(2)	−615(4)	163(3)
C468	130(2)	−619(3)	4(2)
C560	97(2)	−197(4)	120(2)
C561	142(1)	−69(3)	142(2)
C562	163(2)	−58(3)	197(2)
C563	179(2)	35(3)	209(2)
C564	171(2)	88(3)	167(2)
C565	146(3)	80(5)	114(3)
C566	128(2)	−14(3)	99(2)
C567	178(2)	−120(3)	242(2)
C568	100(2)	−32(4)	42(2)

[a] Positional parameters were multiplied by 10^4.

The positions of one Hg and six Pt atoms were determined by direct methods using the program MULTAN. The other atomic positions were subsequently found from a series of different Fourier maps [18]. The positions of one Hg and six Pt atoms were refined anisotropically and those of the other atoms isotropically by using block-diagonal least-squares methods, minimizing $\Sigma w(|F_o|-|F_c|)^2$. The refinement converged to $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ of 0.099 and 0.120, respectively. At this step, an absorption correction was made. The absorption coefficient is 114.3 cm^{-1}, and the calculated transmission factors varied from 0.09 to 0.047. A further five cycles of refinement converged to $R=0.048$ and $R_w=0.054$ ($w=1$). A final different Fourier map showed no residual peaks greater than 2.0 e $Å^{-3}$ around the heavy atoms and no residual peaks greater than 0.8 e $Å^{-3}$ associated with the light atoms. No attempt was made to locate the hydrogen atoms. Anomalous dispersion effects were included in the calculations of F_c by using $\Delta f'$ and $\Delta f''$ [19]. The atomic scattering factors for Pt, Hg, N and C atoms were from the usual tabulation [20]. Crystal data and data collection, and the final atomic coordinates are listed in Tables 4 and 5. See also 'Supplementary material'.

X-ray photoelectron spectra

A typical preparation of a sample was to make a solution of the sample complex in benzene and to deposit a thin uniform film of the liquid solution onto pure Au sheets, whose surface was then allowed to evaporate to dryness. X-ray photoelectron spectra were obtained with a Hewlett-Packard 5950A photoelectron spectrometer with monochromatized Al Kα X-rays (1486.6 eV). Spectrometer pressure was at the level of 10^{-9} torr. The binding energy scale was calibrated to the Au $4f_{7/2}$ peak (84.0 eV).

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Supplementary material

A listing of additional bond distances, angles, least-squares planes, thermal parameters, and tables of observed and calculated structure factors are available from the authors.

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Appendix

The parameters used in the EHMO calculations were from ref. 21. The Pt–Pt, Pt-Hg, Pt–C(terminal) and Pt–C(bridged) distances were set to 2.64, 2.96, 1.92 and 2.09 Å, respectively. All C≡N, C=N and N–H distances were set to 1.17, 1.21 and 1.01 Å, respectively. The C(bridged)–N–H angle was set to 120 and Pt–Pt–C(terminal), to 150°. The Pt–C(terminal)–N, C(terminal)–N–H bond angles were idealized to be linear.