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$PtAu_8Hg_2$ and $PtAu_7Hg_2$ Cluster Compounds. X-ray Structure of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4 \cdot 3CH_2Cl_2$

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Salts of the cations $[Pt(AuPPh_3)_8(HgX)_2]^{2+}$, $[Pt(AuPPh_3)_7(AuX)(HgX)_2]^+$, and $[Pt(AuPPh_3)_7(HgX)_2]^+$ (X = NO_3, Cl) were prepared by reaction of salts of $[Pt(AuPPh_3)_8]^{2+}$ with Hg_2X_2 or HgX_2. The clusters were characterized by ^{31}P and ^{195}NMR spectroscopy, IR spectroscopy, and conductivity measurements. The crystal and molecular structure of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4 \cdot 3CH_2Cl_2$ has been determined by X-ray analysis. The compound crystallizes in space group $P4/n$, with $a = 17.8002$ (6) Å, $c = 23.0493$ (13) Å, $V = 7303$ Å^3, and $Z = 2$. Cu Kα radiation was used. The residuals are $R = 0.039$ and $R_w = 0.060$ for 5936 observed reflections and 371 variables. The metal frame of approximately D_{4d} symmetry is a centered square antiprism, capped on the squares. The Pt is in the center and is surrounded by eight $AuPPh_3$ groups and two Hg atoms, the Au atoms being on the vertices of the squares and the Hg on the caps. The steric strain of the eight PPh_3 and two NO_3 groups in the periphery of $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$ is relieved by loss of NO_3 from both Hg atoms, by substitution of one of the eight Au-bonded PPh_3 groups by NO_3, or by dissociation of a $AuPPh_3^+$ ion.

Introduction

Reaction of mercuric compounds, HgX_2, with transition-metal complexes leads to the formation of metal–mercury bonds,[1] either by an oxidative addition reaction[2-4]

$$Pt(PPh_3)_3 + HgX_2 \rightarrow Pt(PPh_3)_2(X)(HgX) + PPh_3$$

or by a donor–acceptor reaction[5-7]

$$Co(CO)(\pi\text{-}C_5H_5) + HgX_2 \rightarrow Co(CO)(\pi\text{-}C_5H_5)(HgX_2)$$

With metal clusters, electron-deficient $\mu 2$, $\mu 3$, and $\mu 4$ transition metal–mercury bonds are formed.[8] We are studying $Pt(AuPPh_3)_n$ clusters and have discovered that the reactivity of these clusters resembles the reactivity of mononuclear platinum compounds in electrophilic, nucleophilic, and oxidative additions.[9-12] We reported preliminary results of the reactivity of the $Pt(AuPPh_3)_8{}^{2+}$ cluster toward HgX_2 and $(HgX)_2$.[13] Here we report the preparation, characterization, and interconversion of different $PtAu_nHg_2$ cluster compounds and the structure determination of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4 \cdot 3CH_2Cl_2$.

Experimental Section

Analyses were carried out at the microanalytical department of the University of Nijmegen and by Dr. A. Bernhardt, Elbach über Engelskirchen, FRG. ICP Analyses giving Pt:Au:P ratios were carried out on a Plasma 200 ICP A-E spectrometer in DMSO solutions with $Pt(AuPPh_3)_8(NO_3)_2$ as reference. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM 200 spectrometer at 81.02 MHz and on a Bruker CPX 300 spectrometer at 121.44 MHz with CH_2Cl_2 solutions and TMP/CD_2Cl_2 as external reference. $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker WM 200 spectrometer at 43.02 MHz in CD_2Cl_2 solutions with K_2PtCl_6 in D_2O as external references. The IR spectra of CsI pellets were recorded on a Perkin-Elmer 1720-X infrared Fourier transform spectrometer. The conductivity measurements were carried out with a Metrohm E365 Konduktoskop.

Preparation. $[Pt(AuPPh_3)_8](NO_3)_2$ and $[Pt(AuPPh_3)_8](PF_6)_2$ were prepared according to the literature.[11] All solvents were of reagent grade and were used without further purification.

$[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$. (1) A solution of 100 mg (0.025 mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in 25 mL of acetone is added to a suspension of 15 mg (0.025 mmol) of $[Hg_2(H_2O)_2](NO_3)_2$ in 100 mL of acetone. The reaction mixture is stirred for 24 h and evaporated to dryness. The dark red-brown solid is dissolved in CH_2Cl_2. The red solution is filtered and evaporated to dryness, yielding an orange solid. This is washed with diethyl ether and dried in vacuo. Yield: 60 mg (0.013 mmol).

(2) To a solution of 100 mg (0.025 mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in 50 mL of acetone is added a suspension of 8 mg (0.025 mmol) of $Hg(NO_3)_2$ in 35 mL of acetone. After 5 h of stirring, the acetone solution is evaporated to dryness. The red-brown solid is dissolved in 50 mL of methanol, and the solution is filtered. Yellow crystals are formed within 3 days by slow diffusion of diethyl ether into the methanol solution. Yield: 10 mg (0.002 mmol). Anal. Calcd for $PtAu_8Hg_2P_8C_{144}H_{120}N_4O_{12}$ (mol wt 4518.38): C, 38.28; H, 2.68; N, 1.24. Found: C, 37.01; H, 2.68; N, 1.17. IR: 1260 and 1465 cm^{-1} (coordinated NO_3^-), 1360 cm^{-1} (free NO_3^-). ^{31}P NMR: $\delta = 58.4$ ppm ($^2J(^{195}Pt-^{31}P) = 406$ Hz, $^3J(^{199}Hg-^{31}P) = 471$ Hz). ^{195}Pt NMR: $\delta = -6301$ ppm (nonet) ($^2J(^{195}Pt-^{31}P) = 408$ Hz, $^1J(^{199}Hg-^{195}Pt) = 9350$ Hz).

$[Pt(AuPPh_3)_8Hg_2](NO_3)_4 \cdot 3CH_2Cl_2$. A 5-mg sample of $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$ is dissolved in 1 mL of a methanol/CH_2Cl_2 (5/1) mixture. By slow diffusion of diethyl ether, yellow needles and red cubes are formed. IR (yellow needles, $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$): 1465 and 1260 cm^{-1} (coordinated nitrate), 1360 cm^{-1} (free NO_3^-). IR (red cubes, $[Pt(AuPPh_3)_8Hg_2](NO_3)_4 \cdot 3CH_2Cl_2$): 1360 cm^{-1} (free NO_3^-). These bars were suitable for X-ray analysis. The solvent content was established by X-ray analysis.

$[Pt(AuPPh_3)_8(HgNO_3)_2](PF_6)_2$ can be prepared in the same way as $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$, starting with 100 mg (0.026 mmol) of $[Pt(AuPPh_3)_8](PF_6)_2$ and 14 mg (0.025 mmol) of $[Hg_2(H_2O)_2](NO_3)_2$. Recrystallization takes place from a CH_2Cl_2/methanol (5/1) solution by slow diffusion of diethyl ether. The yellow crystals are filtered off, washed with diethyl ether, and dried in vacuo. Yield: 70 mg (0.015 mmol). Anal. Calcd for $PtAu_8Hg_2P_{10}C_{144}H_{120}N_2O_6F_{12}$ (mol wt 4684.28): C, 36.92; H, 2.63; N, 0.60. Found: C, 36.55; H, 2.63; N, 0.66. ICP: Pt:Au:P = 1.02:8.0:9.91. IR: 1260 and 1465 cm^{-1} (coordinated NO_3^-), 840 cm^{-1} (free PF_6^-). ^{31}P NMR: $\delta = 58.4$ ppm ($^2J(^{195}Pt-^{31}P) = 406$ Hz, $^3J(^{199}Hg-^{31}P) = 471$ Hz). ^{195}Pt NMR: $\delta = -6301$ ppm

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† University of Nijmegen.

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(1) Burlitch, J. M. In *Comprehensive Organometalic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 6, Chapter 4.

(2) Nijholm, R. S.; Vrieze, K. *J. Chem. Soc.* **1965**, 5337.

(3) Layton, A. J.; Nijholm, R. S.; Pneumaticakis, G. A.; Tobe, M. L. *Chem. Ind.* **1967**, 465.

(4) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.

(5) Nowell, I. W.; Russel, D. R. *J. Chem. Soc., Dalton Trans.* **1972**, 2393.

(6) Brooks, P. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 783.

(7) v. d. Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L.; Duisenberg, J. M. *Organometallics* **1982**, *1*, 1066.

(8) Dean, P. A. W. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, Chapter 11.

(9) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Behm, H. J.; Steggerda, J. J. *Inorg. Chem.* **1988**, *27*, 4034.

(10) Kanters, R. P. F.; Schlebos, P. P. J.; Bour, J. J.; Bosman, W. P.; Smits, J. M. M.; Beurskens, P. T.; Steggerda, J. J. Submitted for publication in *Inorg. Chem.*

(11) Bour, J. J.; Kanters, R. P. F.; Schlebos, P. P. J.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 211.

(12) Bour, J. J.; Kanters, R. P. F.; Schlebos, P. P. J.; Bosman, W. P.; Behm, H.; Beurskens, P. T. Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 157.

(13) Kanters, R. P. f.; Bour, J. J.; Schlebos, P. P. J.; Steggerda, J. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1634.

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(nonet) ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 408 Hz (Hg–Pt coupling not detected)).

$[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]NO_3$. (1) A solution of 100 mg (0.025 mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in 25 mL of acetone is added to a suspension of 10 mg (0.030 mmol) of $Hg(NO_3)_2$ in 100 mL of acetone. The mixture is stirred for 24 h and evaporated to dryness. The brown-red solid is dissolved in CH_2Cl_2, and the solution is filtered. The solution is evaporated to dryness, giving a brown-red oil. This oil is dissolved in 1 mL of methanol, after which a bright orange solid precipitates. This is filtered off and washed four times with 0.5 mL of methanol and finally with diethyl ether. The product can be recrystallized by slow diffusion of toluene into a dichloromethane solution. The crystals are filtered off, washed with diethyl ether, and dried in vacuo. Yield: 55 mg (0.012 mmol).

(2) A solution of 100 mg (0.025 mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in 5 mL of methanol is added to a suspension of 15 mg (0.025 mmol) of $[Hg_2(H_2O)_2](NO_3)_2$ in 10 mL of methanol. During 24 h of stirring an orange precipitate is formed. The precipitate is filtered off and dissolved in dichloromethane. After filtration, diethyl ether is added for crystallization. Yield: 10 mg (0.002 mmol).

(3) To a solution of 50 mg (0.011 mmol) of $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$ in 1 mL of methanol is added 13 mg (0.025 mmol) of $AuPPh_3NO_3$. Within 5 min an orange precipitate is formed. The precipitate is filtered off and recrystallized as orange needles from a dichloromethane solution by slow diffusion of diethyl ether. Yield: 35 mg (0.008 mmol). Anal. Calcd for $PtAu_8Hg_2P_7C_{126}H_{105}N_4O_{12}$ (mol wt 4256.07): C, 35.56; H, 2.49; N, 1.32. Found: C, 35.23; H, 2.48; N, 1.26. ICP: Pt:Au:P = 1.03:8.0:7.17. Conductivity (in acetone at 25 °C): Λ_0 = 144 cm^2 Ω^{-1} mol^{-1}. IR: 1260 and 1465 cm^{-1} (coordinated NO_3^-), 1360 cm^{-1} (free NO_3^-). ^{31}P NMR: δ = 58.2 ppm ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 394 Hz, $^{3}J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 545 Hz). ^{195}Pt NMR: δ = −6761 ppm (octet) ($^{2}J(^{31}\mathrm{P}-^{195}\mathrm{Pt})$ = 395 Hz, $^{1}J(^{199}\mathrm{Hg}-^{195}\mathrm{Pt})$ = 10 370 Hz).

$[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]PF_6$. To a solution of 50 mg of $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2](NO_3)$ in 3 mL of CH_2Cl_2 is added a solution of 25 mg of NEt_4PF_6 in 50 mL of ethanol. Within 30 min orange needles are formed. The needles are filtered off, washed with three portions of 5 mL of ethanol, and dried in vacuo. Anal. Calcd for $PtAu_8Hg_2P_8C_{126}H_{105}N_3O_9F_6$ (mol wt 4421.99): C, 34.85; H, 2.48; N, 0.97. Found: C, 34.91; H, 2.46; N, 0.90. ICP: Pt:Au:P = 1.01:8.0:7.9. IR: 1260 and 1465 cm^{-1} (coordinated NO_3^-), 840 cm^{-1} (free PF_6^-). ^{31}P NMR: δ = 58.2 ppm ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 394 Hz, $^{3}J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 545 Hz).

$[Pt(AuPPh_3)_8(HgCl)_2](NO_3)_2$. A solution of 100 mg (0.025 mmol) of $[Pt(AuPPh_3)_8](NO_3)_2$ in 25 mL of acetone is added to a suspension of 17 mg of Hg_2Cl_2 (0.036 mmol) in 100 mL of acetone. The mixture is stirred for 24 h and is then evaporated to dryness. The brown solid is dissolved in dichloromethane, and the solution is filtered. $[Pt(AuPPh_3)_8(HgCl_2)](NO_3)_2$ is crystallized by slow diffusion of toluene into the dichloromethane solution. Yield: 80 mg (0.018 mmol). Anal. Calcd for $PtAu_8Hg_2P_8C_{144}H_{120}N_2O_6Cl_2$ (mol wt 4465.27): C, 38.73; H, 2.71; N, 0.63. Found: C, 36.96; H, 2.66; N, 0.54. ICP: Pt:Au:P = 1.02:8.0:7.81. Conductivity (in acetone at 25 °c): Λ_0 = 197 cm^2 Ω^{-1} mol^{-1} IR: 1360 cm^{-1} (free NO_3^-), 275 cm^{-1} (HgCl). ^{31}P NMR: δ = 57.8 ppm ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 395 Hz, $^{3}J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 356 Hz).

$[Pt(AuPPh_3)_7(AuCl)(HgCl)_2]NO_3$. To a solution of 100 mg (0.022 mmol) of $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]NO_3$ in 5 mL of CH_2Cl_2 is added 40 mg (0.22 mmol) of NEt_4Cl. The solution is evaporated to dryness after 2 h of stirring. The orange solid is recrystallized by slow diffusion of methanol into a CH_2Cl_2 solution. Yield: 75 mg (0.017 mmol). ICP: Pt:Au:P = 1.03:8.0:7.03. ^{31}P NMR: δ = 57.3 ppm ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 386 Hz, $^{3}J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 406 Hz).

$[Pt(AuPPh_3)_7(AuCl)(HgCl)_2]PF_6$. To a solution of 100 mg (0.022 mmol) of $[Pt(AuPPh_3)_7(AuCl)(HgCl_2)]NO_3$ in 5 mL of CH_2Cl_2 is added a solution of 30 mg of KPF_6 in 5 mL of methanol. The mixture is evaporated to dryness and dissolved in CH_2Cl_2, and the solution is filtered. Crystallization takes palce by slow diffusion of methanol into the CH_2Cl_2 solution. Yield: 100 mg (0.021 mmol). Anal. Calcd for $PtAuP_8Hg_2P_8C_{126}H_{105}Cl_3F_6$ (mol wt 4256.07): C, 35.53; H, 2.28. Found: C, 35.31; H, 2.47. IR: 840 cm^{-1} (free PF_6^-); 278 cm^{-1} (HgCl and AuCl). Conductivity (in acetone at 25 °C): Λ_0 = 130 cm^2 Ω^{-1} Mol^{-1}. ^{31}P NMR: δ = 57.3 ppm ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 386 Hz, $^{3}J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 406 Hz). ^{195}Pt NMR: δ = −6560 ppm (octet) ($^{2}J(^{31}\mathrm{P}-^{195}\mathrm{Pt})$ = 386 Hz $^{1}J(^{199}\mathrm{Hg}-^{195}\mathrm{Pt})$ = 8890 Hz).

$[Pt(AuPPh_3)_7(HgNO_3)_2]NO_3$. From a solution of 50 mg of $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$ in 10 mL of a methanol/diethyl ether mixture (3/7) crystallizes 10 mg of $[Pt(AuPPh_3)_7(HgNO_3)_2]NO_3$ within 2 weeks. The crystals are filtered off, washed with diethyl ether, and dried in vacuo. Anal. Calcd for $PtAu_7Hg_2P_7C_{126}H_{105}N_3O_9$ (mol wt 3997.11): C, 37.86; H, 2.65; N, 1.05. Found: C, 36.78; H, 2.68; N, 1.02. ICP: Pt:Au:P = 1.03:7.0:7.32. IR: 1263 and 1452 cm^{-1} (coordinated NO_3^-); 1360 cm^{-1} (free NO_3^-). ^{31}P NMR: δ = 57.2 ppm ($^{2}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$ = 471 Hz, $^{3}J(^{199}\mathrm{Hg}-^{31}\mathrm{P})$ = 580 Hz). An alternative quick synthesis with a larger yield, but with an impurity of $Au(PPh_3)_2^+$, is as follows. To a solution of 100 mg (0.022 mmol) of $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$ in 10 mL of ethanol is added 10 mg (0.036 mmol) of triphenylphosphine. Within 10 min the reaction is completed and $[Pt(AuPPh_3)_7(HgNO_3)_2]^+$ and $Au(PPh_3)_2^+$ are the only products seen in ^{31}P NMR spectrum. Purification, however, was not successful.

Table I. Crystal Data for $[Pt(AuP(C_6H_5)_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$

chem formula	$C_{147}Cl_6H_{126}N_4O_{12}P_8PtAu_8Hg_2$
fw	4773.1
a	17.8002 (6) Å
c	27.88 (3) Å
V	7303 Å^3
Z	2
space group	$P4/n$ (No. 85, origin choice 2)
T	20 °C
λ	1.541 838 Å
ρ_{calc}	2.171 g/cm^3
μ(Cu Kα)	229.76 cm^{-1}
$R(F_o)$	0.039
$R_w(F_o)$	0.060

Structure Determination of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl$. Collection and Reduction of Crystallographic Data. Since single crystals decomposed very quickly upon removal from the mother liquor, a crystal of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$ was mounted in a capillary together with a mixture of dichloromethane and diethyl ether. X-ray data were measured on a Nonius CAD4 diffractometer. Standard experimental and computational details are given elsewhere.[14] The crystal data are listed in Table I. No extinction correction was performed.

Solution and Refinement of the Structure. The positions of the metal atoms were found by automated Patterson interpretation (PATSYS[15]) and direct-method fragment expansion (DIRDIF[15]). The remaining non-hydrogen atoms were positioned from successive difference Fourier maps. The structure was refined by full-matrix least-squares techniques using SHELX.[15] All H atoms were introduced at expected positions and refined in the riding mode (C–H = 0.98 Å). One overall isotropic temperature factor (U = 0.078 (7) Å^2) was used for all H atoms. Anisotropic parameters were used for the non-hydrogen cluster atoms. The eight NO_3^- ions in the unit cell (one independent) could not be located. At this stage (R = 0.049) a difference Fourier map showed various peaks in four regions (numbered 1–4) and near some of the heavy atoms. The latter peaks were assumed to be absorption effects. Neither NO_3^- ions nor solvent molecules could be fitted on the electron density in the regions mentioned above. The BYPASS procedure[16] then was used to take these electron densities into account in the full-matrix least-squares refinement. Region 1, located around a site with 4 symmetry ($^3/_4$, $^1/_4$, 0), has a volume of 213 Å^3, and the integrated electron density for this area is 60 electrons. This volume is reasonably close to the expected (about 2 × 80 Å^3) volume of two NO_3^- ions, and the number of electrons is in excellent agreement ($2NO_3^-$ = 64 electrons). Region 2 is symmetry-related to region 1. Region 3, located around a site at the 4-fold rotation axis ($^1/_4$, $^1/_4$, 0.8), has a volume of 446 Å^3 and contains 190 electrons. In view of the high mean electron density (0.42 e/Å^3), it must be a solvent containing heavy atoms such as Cl. These data agree with the presence of two NO_3^- and three CH_2Cl_2 groups (volume about 2 × 80 + 3 × 120 Å^3; 190 electrons). Region 4 is symmetry-related with region 3. The Fourier map calculated with the continuous solvent contribution to the calculated structure factors is consistent with the presence of two NO_3^- ions, each disordered by its position on the 2-fold axis. The electron density visible in the Fourier map (Figure 1) does not contradict the presence of two NO_3^- ions and three dichloromethane molecules, disordered by the 4-fold axis. The total of eight NO_3^- ions in the unit cell, known from the chemical evidence, is the basis of the result that there are six dichloromethane molecules present. Final covergence was reached at R = 0.039. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1.767/[\sigma^2(F_o) + 0.02715F_o^2]$ for 5936 reflections. Maximum shift/esd = 0.14; number of refined parameters = 371. Maximum residual density was 2.6 e/Å^3 near the Pt and Hg atoms. Further residual density was below 0.9 e/Å^3.

Results

Crystal Structure of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$. Selected final positional parameters are given in Table II. Selected

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(14) Smits, J. J. M.; Behm, H.; Bosman, W. P.; Beurskens, P. T. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 447.

(15) Computer program references for PATSYS (Behm, Beurskens), DIRDIF (Beurskens et al.), and SHELX (Sheldrick) are listed in ref 14.

(16) van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A*, in press.

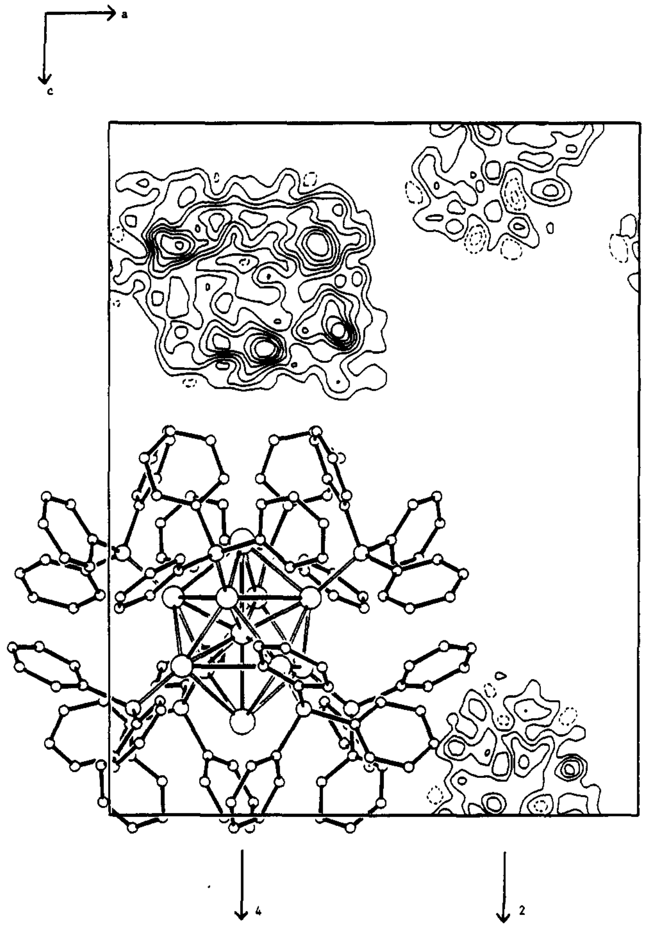

Figure 1. Projection of one molecule along *b*(24) superimposed with the section at $y = 0.183$ of the Fourier synthesis calculated for the area with the continuous solvent electron density (contour levels at 0.2 e/Å^3, minimum −0.3 e/Å^3, maximum 1.5 e/Å^3). The position of the 4- and 2-fold rotation axis at $Y = 0.25$ are indicated.

Table II. Selected Fractional Positional and Thermal Parameters for $[Pt(AuP(C_6H_5)_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$

atom	x	y	z	10^2U_{eq},^{a} Å^2
Pt(1)	0.25000	0.25000	0.26210 (2)	1.48 (1)
Hg(1)	0.25000	0.25000	0.13506 (3)	3.72 (2)
Hg(2)	0.25000	0.25000	0.39422 (3)	3.68 (2)
Au(1)	0.32166 (2)	0.13645 (2)	0.21423 (1)	2.90 (1)
Au(2)	0.22211 (2)	0.12089 (2)	0.31329 (1)	2.66 (1)
P(1)	0.3661 (1)	0.0440 (1)	0.15386 (9)	3.95 (7)
P(2)	0.2009 (1)	0.0251 (1)	0.37742 (8)	3.08 (6)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j a^*_i a^*_j a_i a_j U_{ij}$.

interatomic distances and angles are collected in Table III. The molecular structure together with the crystallographic numbering scheme is given in Figure 2.

The X-ray structure determination of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$ shows that the $PtAu_8Hg_2$ skeleton, with a crystallographic 4-fold rotation axis, is a centered square antiprism capped on the square faces, with approximately D_{4d} symmetry (Figure 2). The NMR data indicate that Pt is in the center and the metal atoms connected to P are Au; the two trans atoms standing on the C_4 axis are thus Hg. The metal frame is closely related to the centered square-antiprismatic frame of the parent compound $[Pt(AuPPh_3)_8]^{2+}$, the squares are now capped by Hg. The Pt–Hg and the Au–Hg bonds are of the same magnitude, averaging 2.98 and 3.00 Å, respectively. The Pt–Hg bonds are long compared with those found in dinuclear Pt–Hg compounds (2.71–2.83 Å),[17,18] but comparable with those found in Pt_3Hg clusters (average 2.99 Å).[19,20] The Au–Au bonds between the two squares (Au(1)–Au(2)) are lengthened from 2.827 Å[11] in $[Pt(AuPPh_3)_8]^{2+}$ to 2.91 Å (average) in the $PtAu_8Hg_2$ cluster. They are in the range found for peripheral Au–Au bond distances in Pt–Au cluster compounds.[10,11] The Au–Au distances in the squares Au(1)–Au(1) and Au(2)–Au(2) are long (3.38–3.32 Å) but are in the range found for the parent compound.[11] A Pt–Au distance of 2.63 Å is found in $PtAu_8Hg_2$ as well as in $[Pt(AuPPh_3)_8]^{2+}$.[11] The Au–P bond lengths (average 2.29 Å) are in the range normally found in gold clusters. The P(1) atoms bend away from the P(2) atoms (Pt–Au–P = 166.3°) probably due to steric hindrance. The two Hg atoms have, apart from Au and Pt, no close contacts either with NO_3 or with any solvent molecule that is included in the crystal; this is in accordance with the IR spectrum, which shows only free NO_3^- ions present.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Pt(AuP(C_6H_5)_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$ (with Esd's)

Pt–Hg(1)	2.9282 (8)	Au(2)–Au(2)′	3.3251 (4)
Pt–Hg(2)	3.0453 (9)	Au(1)–P(1)	2.295 (2)
Pt–Au(1)	2.6324 (4)	Au(2)–P(2)	2.289 (2)
Pt–Au(2)	2.6307 (4)	P(1)–C(116)	1.813 (9)
Hg(1)–Au(1)	3.0070 (5)	P(1)–C(126)	1.85 (1)
Hg(2)–Au(2)	3.0011 (5)	P(1)–C(136)	1.81 (1)
Au(1)–Au(1)′	3.3800 (1)	P(2)–C(216)	1.832 (9)
Au(1)–Au(2)	2.9036 (4)	P(2)–C(226)	1.833 (9)
Au(1)–Au(2)′	2.9298 (4)	P(2)–C(236)	1.811 (8)

Hg(1)–Pt–Hg(2)	180.00	Pt–Au(2)–Au(1)	56.55 (1)
Hg(1)–Pt–Au(1)	65.22 (1)	Hg(1)–Au(1)–Au(2)	106.41 (1)
Hg(1)–Pt–Au(2)	116.65 (1)	Hg(2)–Au(2)–Au(1)	108.35 (1)
Hg(2)–Pt–Au(1)	114.78 (1)	Pt–Au(1)–P(1)	166.26 (5)
Hg(2)–Pt–Au(2)	63.35 (1)	Pt–Au(2)–P(2)	166.43 (5)
Au(1)–Pt–Au(2)	66.97 (1)	Hg(1)–Au(1)–P(1)	105.08 (5)
Au(1)–Pt–Au(1)′	79.88 (1)	Hg(2)–Au(2)–P(2)	101.35 (5)
Au(1)–Pt–Au(2)′	67.65 (1)	Au(2)–Au(1)–P(1)	128.21 (5)
Au(2)–Pt–Au(2)′	78.39 (1)	Au(1)–Au(2)–P(2)	132.83 (5)
Pt–Hg(1)–Au(1)	52.64 (1)	Au(1)–P(1)–C(126)	111.4 (4)
Pt–Hg(2)–Au(2)	51.58 (1)	Au(1)–P(1)–C(116)	112.0 (3)
Au(1)–Hg(1)–Au(1)	68.39 (1)	Au(1)–P(1)–C(136)	117.2 (3)
Au(2)–Hg(2)–Au(2)	67.28 (1)	Au(2)–P(2)–C(216)	113.8 (3)
Pt–Au(1)–Hg(1)	62.14 (1)	Au(2)–P(2)–C(226)	115.4 (3)
Pt–Au(2)–Hg(2)	65.08 (1)	Au(2)–P(2)–C(236)	113.4 (3)
Pt–Au(1)–Au(2)	56.49 (1)		

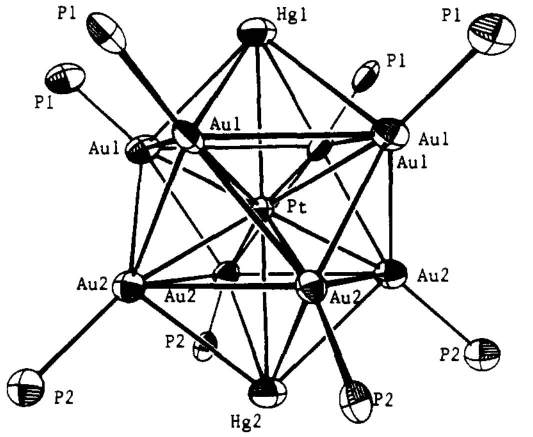

Figure 2. X-ray structure of $[Pt(AuPPh_3)_8Hg_2](NO_3)_4{\cdot}3CH_2Cl_2$. Phenyl groups and the NO_3^- are omitted for the sake of clarity. Thermal ellipsoids are at 50% probability.

$[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$. The reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with $[Hg_2(H_2O)_2](NO_3)_2$ leads, with about 50% yield, to the formation of $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$. With $Hg(NO_3)_2$, the same compound is formed but with 10% yield. In the IR spectrum the vibrational frequencies of free NO_3^-

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(17) Sharp, P. R. *Inorg. Chem.* **1986**, *25*, 4185.

(18) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014.

(19) Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329.

(20) Albinati, A.; Moor, A.; Pregosin, P. S.; Venanzi, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 7672.

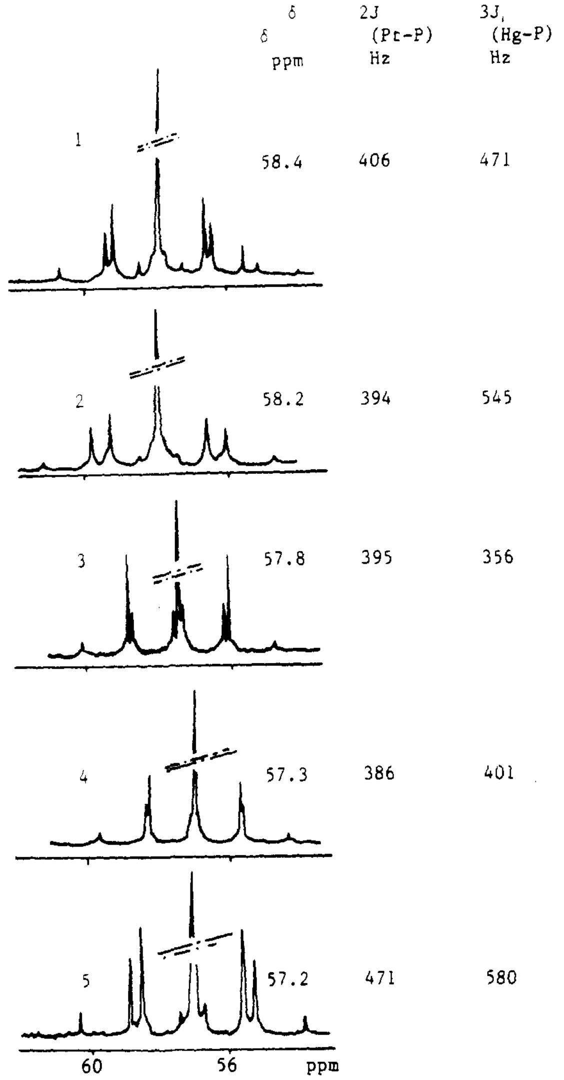

Figure 3. $^{31}P\{^1H\}$ NMR spectra of **1**–**5**: **1** = $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$; **2** = $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+$; **3** = $[Pt(AuPPh_3)_8(HgCl)_2]^{2+}$; **4** = $[Pt(AuPPh_3)_7(AuCl)(HgCl)_2]^+$; **5** = $[Pt(AuPPh_3)_7(HgNO_3)_2]^+$.

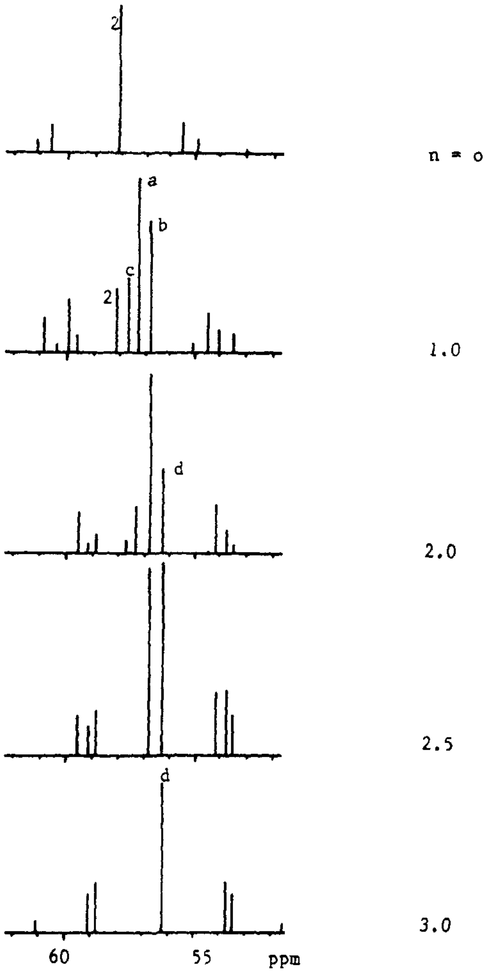

Figure 4. $^{31}P\{^1H\}$ NMR stick spectra of the reaction of **2** with different amounts of Cl^- ($n = [Cl^-]/[\mathbf{2}]$; **2** = $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+$).

(1360 cm^{-1}) and coordinated NO_3^- (1465 and 1260 cm^{-1}) are present. With $[Pt(AuPPh_3)_8](PF_6)_2$, $[Pt(AuPPh_3)_8(HgNO_3)_2](PF_6)_2$ can be prepared, while the IR spectrum reveals coordinated NO_3^- and free PF_6^-. So in this cluster ion the Hg atoms are coordinated to NO_3^-, this in contrast with the case of $[Pt(AuPPh_3)_8Hg_2]^{4+}$. However, the molar conductivity in acetone solution is very high. As Λ vs $C^{1/2}$ is curved, extrapolation to infinite dilution is difficult, but Λ_∞ seems to be about 500 cm^2 Ω^{-1} mol^{-1}. This indicates that in acetone solution the cluster ion $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$ is dissociated for a great part into $[Pt(AuPPh_3)_8Hg_2]^{4+}$ and NO_3^- ions. More structural information stems from the ^{31}P and ^{195}Pt NMR spectra. The different isotopomers in combination with their relative intensities in the ^{31}P NMR spectra (Figure 3) indicate the presence of one Pt and two Hg atoms ($^2J(^{195}Pt-^{31}P)$ = 406 Hz, $^3J(^{199}Hg-^{31}P)$ = 471 Hz). The ^{195}Pt NMR spectrum shows a central nonet $\delta = -6301$ ppm, $^2J(^{31}P-^{195}Pt)$ = 408 Hz, and two Hg satellites, $^1J(^{199}Hg-^{195}Pt)$ = 9350 Hz. The nonet indicates the presence of eight equivalent $AuPPh_3$ groups. The magnitudes of the Pt–P, Hg–P, and Hg–Pt coupling constants indicate that they are ^2J(Pt–P), ^3J(Hg–P), and ^1J(Hg–Pt), respectively. All these data are in accord with the proposed structure $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$, very similar to that found for the $[Pt(AuPPh_3)_8Hg_2]^{4+}$ cluster ion, with Pt in the center of the cluster, bonded to the eight $AuPPh_3$ groups and two $HgNO_3$ groups.

$[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+$. When a phosphine scavenger such as $AuPPh_3NO_3$ is added to a solution of $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$ in methanol, $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+$ is formed and isolated as its nitrate salt in 70% yield. The product is also obtained in low yields from a concentrated methanol solution of $[Pt(AuPPh_3)_8](NO_3)_2$ with $[Hg_2(H_2O)_2](NO_3)_2$. When $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]NO_3$ is treated with NH_4PF_6, $[Pt(Au_8PPh_3)_7Hg_2(NO_3)_3]PF_6$ precipitates. The IR spectrum shows that NO_3^- is coordinated and PF_6^- is free.

Different isotopomers (Figure 3) in combination with their relative intensities in the ^{31}P NMR spectra indicate the presence of one Pt and two Hg atoms. The ^{195}Pt NMR spectrum shows an octet, $^2J(^{31}P-^{195}Pt)$ = 395 Hz, indicating the presence of seven Au–P groups, while the Hg–Pt coupling of 10 360 Hz indicates Hg–Pt bonding. These NMR data in combination with the IR data and elemental analysis indicate that Pt is in the center, surrounded by seven AuP groups, one $AuNO_3$ group, and two $HgNO_3$ groups bonded to Pt by Au and Hg, respectively. In the PF_6 salt only free nitrate is substituted.

$[Pt(AuPPh_3)_8(HgCl)_2](NO_3)_2$. $[Pt(AuPPh_3)_8(HgCl)_2](NO_3)_2$ is formed with 70% yield in the reaction of $[Pt(AuPPh_3)_8](NO_3)_2$ with Hg_2Cl_2. The synthetic route and the NMR data compared with those of $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$ and $[Pt(AuPPh_3)_7(HgNO_3)_2(AuNO_3)]^+$ and the IR spectrum (coordinated Cl^- and free NO_3^-), elemental analysis, and conductivity measurements (2:1 electrolyte) are in agreement with the formulation of $[Pt(AuPPh_3)_8(HgCl)_2]^{2+}$ for the cluster cation.

$[Pt(AuPPh_3)_7(AuCl)(HgCl)_2]NO_3$. $[Pt(AuPPh_3)_7(AuCl)(HgCl)_2]^+$ is formed by adding 3 equiv of Cl^- to $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+$. It can be transformed to its PF_6^- salt by precipitation with KPF_6. The reaction with Cl^- was followed by ^{31}P NMR spectroscopy (see Figure 4). With 1 equiv of Cl^-, $[Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+$ nearly disappears and three new products, a, b, and c, are formed. With 2 equiv of Cl^-, a, b, c, and a new product d are seen. With 2.5 equiv of Cl^-, a and c disappear and b and d now have the same intensities. With ≥3 equiv of Cl^-, d is the only product. Elemental analysis, ^{31}P and ^{195}Pt NMR data, conductivity measurements (1:1 electrolyte), and the synthetic route support the formulation of d as the cation $[Pt(AuPPh_3)_7(AuCl)(HgCl)_2]^+$. As after addition of 2.5 equiv of Cl^- only b and d are present, b must be $[Pt(AuPPh_3)_7AuHg_2Cl_2NO_3]^+$ with NO_3 bonded either to Au or to Hg.

$[Pt(AuPPh_3)_7(HgNO_3)_2]NO_3$. Low concentrated methanol solutions of $[Pt(AuPPh_3)_8(HgNO_3)_2](NO_3)_2$ are stable for several days (see Experimental Section). However, after 2 weeks a small amount of $[Pt(AuPPh_3)_7(HgNO_3)_2]NO_3$ is precipitated. $[Pt(AuPPh_3)_7(HgNO_3)_2]^+$ is also formed when phosphine is added to $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$. However, this is not a suitable synthetic route, as separation of the product from $Au(PPh_3)_2^+$ is difficult. The structure of the cluster compound is indicated by elemental analysis, IR spectroscopy (bonded and free nitrate), and NMR data.

Discussion

The reaction

$$[Pt(AuPPh_3)_8]^{2+} + Hg_2X_2 \rightarrow [Pt(AuPPh_3)_8(HgX)_2]^{2+}$$

($X = Cl, NO_3$) increases the coordination number of the central Pt atom and the number of valence electrons of the metal frame by 2, as in oxidative additions of mononuclear Pt compounds. The cluster electron configuration goes from $(s^\sigma)^2(p^\sigma)^4$ to $(s^\sigma)^2(p^\sigma)^6$ with a concomitant change from toroidal into spheroidal symmetry of the metal frame.

The X-ray structure of $[Pt(AuPPh_3)_8Hg_2]^{4+}$ shows that the two Hg atoms are in trans position and the crown configuration of $PtAu_8$ in the parent compound is nearly unaffected. As the Pt–Au frames are highly fluxional, the primary reaction product of the oxidative addition could be different from what is found in the crystalline state. A conclusion about the reaction mechanism seems premature. Synthesis of $[Pt(AuPPh_3)_8(HgX)_2]^{2+}$ using HgX_2 is also possible; however, the yield is low even after prolonged reaction times. A preliminary reduction to Hg_2X_2 might occur in which a part of the $[Pt(AuPPh_3)_8]^{2+}$ is oxidized. The reaction

$$[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+} + 2Cl^- \rightarrow [Pt(AuPPh_3)_8(HgCl)_2]^{2+} + 2NO_3^-$$

is easy. The substitution of one of the Au-bonded phosphines is also rather fast

$$[Pt(AuPPh_3)_8(HgX)_2]^{2+} + X^- \rightarrow [Pt(AuPPh_3)_7(AuX)(HgX)_2]^+ + P$$

($X = NO_3$ or Cl). This is similar to the reaction

$$[Au(AuPPh_3)_8(AuY)_2]^+ + Y^- \rightarrow Au(AuPPh_3)_7(AuY)_3 + P$$

($Y = Cl, SCN$).[23]

The driving force of these reactions is probably the steric crowding of eight triphenylphosphines in combination with a coordination of as high as 10 for the central atom. The steric strain can also be removed by dissociation of one of the $AuPPh_3^+$ groups

$$[Pt(AuPPh_3)_8(HgX)_2]^{2+} \rightleftarrows [Pt(AuPPh_3)_7(HgX)_2]^+ + AuPPh_3^+$$

This is probably an equilibrium that can be shifted to the right by the addition of phosphine, which binds the $AuPPh_3^+$ as $Au(PPh_3)_2^+$.

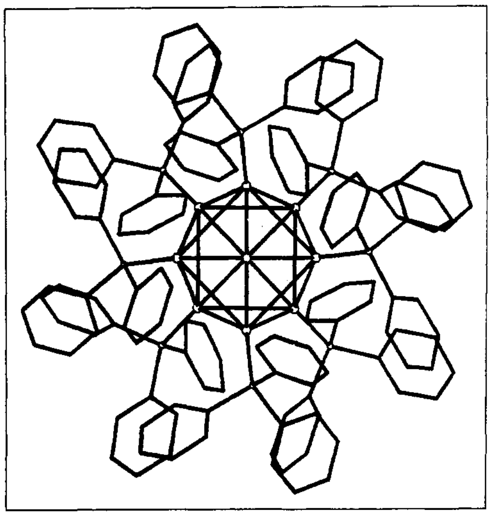

Figure 5. X-ray structure, with phenyl occupation, shown along the Hg–Pt–Hg axis.

The dissociation of $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+}$ into $[Pt(AuPPh_3)_8Hg_2]^{4+}$ and NO_3^- ions in acetone solutions could also be driven by steric crowding. Interestingly, both isomers can be isolated as solid compounds.

The steric strain of the phosphines can be demonstrated by the calculation of the Kitaigirodski packing coefficient,[21] which shows that the maximum number of triphenylphosphines around a metal core as present in Au and Pt–Au clusters is 8.[22,23] The crowding in $Pt(AuPPh_3)_8Hg_2$ is shown in Figure 5. Some narrow corridors are left along the Hg–Pt–Hg axis. When these are filled with NO_3 or Cl, the steric strain is increased considerably.

The rise in coordination number as well as the substitution of NO_3^- by Cl^- on either Hg or Au lowers the Pt–P and Hg–P coupling constants, suggesting a decrease in the metal–metal bonding in the metal core in the orders (a) $[Pt(AuPPh_3)_8(HgNO_3)_2]^{2+} > [Pt(AuPPh_3)_8(HgCl)_2]^{2+}$ and (b) $[Pt(AuPPh_3)_7(HgNO_3)_2]^+ > [Pt(AuPPh_3)_7(AuNO_3)(HgNO_3)_2]^+ > [Pt(AuPPh_3)_7(AuCl)(HgCl)_2]^+$.

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Supplementary Material Available: Tables of crystal data, additional fractional positional parameters, anisotropic temperature factors, and additional bond lengths and angles (4 pages); a listing of structure factors (30 pages). Ordering information is given on any current masthead page.

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(21) Kitaigorodski, A. I. *Organic Chemical Crystallography*; Consultance Bureau: New York, 1961; p 12.
(22) Vollenbroek, F. A.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 137.
(23) Steggerda, J. J.; Bour, J. J.; van der Velden, J. W. A. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 164.
(24) Spek, A. L. *The EUCLID Package. Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, U.K., 1982; p 528.