A linearly coordinated Hg(0) trapped in a gold(I) metallocryptand cage

Vincent J. Catalano,*[a] Mark A. Malwitz[a] and Bruce C. Noll[b]

[a] *Department of Chemistry, University of Nevada, Reno, NV 89557, USA. E-mail: vjc@unr.edu*
[b] *Department of Chemistry, University of Colorado, Boulder, CO 80309, USA*

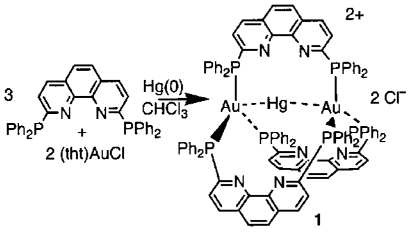
Received (in Irvine, CA, USA) 10th January 2001, Accepted 16th February 2001
First published as an Advance Article on the web 7th March 2001

Hg(0) is effectively encapsulated through strong, closed-shell metallophilic interactions by Au(I)-based metallocryptands using the multidentate P$_2$phen [2,9-bis(diphenylphosphino)-1,10-phenanthroline] ligand; synthesis, characterization and X-ray crystallography are presented.

Even though elemental mercury has found numerous uses and applications in many fields of chemistry, the coordination chemistry of Hg(0) remains extremely limited, and no stable compounds are known where a Hg(0) atom is coordinated to ligands forming a classical coordination compound. Rather, Hg(0) is often found as part of an electron-rich transition metal cluster[1,2] or as an adduct to the face of *triangulo* clusters.[3,4] For example, Puddephatt and coworkers[5] reported the reversible addition of Hg(0) to the trigonal face of $[Pt_3(\mu\text{-CO})(\mu\text{-dppm})_3]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) to form mixed-metal clusters that contain naked, triply bridging Hg(0) atoms. Similarly, Venanzi and coworkers[6] demonstrated that the addition of elemental Hg to $[Pt_3(\mu\text{-CO})_3(PPhPr^i{}_2)_3]$ produces a cluster containing two Pt_3 triangles bridged by a Hg_2 unit. More recently, Puddephatt and coworkers[7,8] extended this motif to generate cage complexes based on the triangular Pt_3 core that are capable of encapsulating metal ions including Hg(0) or Tl(I).

We too, have been investigating the encapsulation of metal ions by inorganic cage complexes denoted as metallocryptands and found a similar affinity for the incarceration of metals with s^2 electronic configurations.[9,10] Recently, we demonstrated that the Au(I)-based metallocryptand employing the ligand 2,9-bis-(diphenylphosphino)-1,10-phenanthroline (P$_2$phen) is a selective host for Tl(I) ion, and the resulting $[Au_2Tl(P_2phen)_3]^{3+}$ complex is intensely luminescent.[11] We have now extended this concept to the encapsulation of elemental Hg and report the structure of the resulting metallocryptate containing an Hg(0) atom in an unusually low coordination mode.

As shown in Scheme 1, the yellow $[Au_2Hg(P_2phen)_3](PF_6)_2$ **1** is readily prepared by reacting a chloroform solution containing 3 equivalents of colorless P$_2$phen with 2 equivalents of Au(tht)Cl (tht = tetrahydrothiophene) and a single drop of elemental mercury.† The chloride salt can be metathesized to the PF_6^- salt using excess $NaPF_6$. Alternatively, **1** can be synthesized by Hg(0) addition to the two-coordinate, gold macrocycle,[11] $[Au_2(P_2phen)_2](PF_6)_2$, and the free ligand in chlorocarbon solution. The $^{31}P\{^1H\}$ spectrum (CD_3CN) of **1** displays a singlet at δ 34.8 with ^{199}Hg satellites ($^2J_{PHg}$ 48 Hz, ^{199}Hg is 16.8% abundant, $I = 1/2$) and a heptet at $\delta -143.7$ that integrates for two PF_6^- anions. The $^{199}Hg\{^1H\}$ NMR spectrum (Fig. 1) displays a septet at δ –1199.8 ($^2J_{HgP}$ 48 Hz) indicating a single Hg environment coupled to six chemically equivalent phosphorus atoms. For comparison, the phosphine environment in **1** is slightly more shielded than that observed in either $[Au_2Tl(P_2phen)_3](PF_6)_3$ or $[Au_2Na(P_2phen)_3](PF_6)_3$ which show resonances at δ 45.7 and 45.5, respectively. As probed by $^{31}P\{^1H\}$ NMR spectroscopy, the Hg atom appears to interact with the AuP_3 center in a fashion similar to the corresponding Tl(I) containing species, as the $^2J_{HgP}$ coupling constant in **1** is closely related to the $^2J_{TlP}$ of 186 Hz observed in $[Au_2Tl(P_2phen)_3](PF_6)_3$ by the simple ratio of the gyromagnetic ratios for ^{199}Hg and ^{205}Tl. Further, $^2J_{HgP}$ coupling constants ranging from 41 to 70 Hz were reported for Hg(0) trapped in the hexaplatinum clusters.[7] No comparable ^{199}Hg NMR chemical shifts could be found for genuine Hg(0) complexes. However, a chemical shift of $\delta -1310$ was reported[12] for the low valent Hg cluster, $[Hg_4](AsF_6)_2$. The chemical shift dispersion for ^{199}Hg is quite large (> 5000 ppm) and is very sensitive to ligation, concentration and temperature.[13] Consistent with other metallocryptates[9] the ^1H NMR spectrum displays single resonances for the three magnetically distinct phenanthroline protons. These signals are only minimally shifted (±0.06 ppm) relative to the uncoordinated ligand. However, two sets of resonances corresponding to phenyl ring protons are observed in the metallocryptate suggesting that two phenyl ring environments exist: one along the metal–metal axis and one equatorial to this axis.



Scheme 1

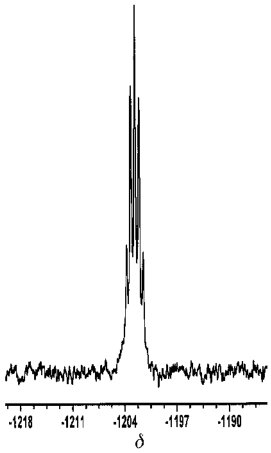


Fig. 1 89.312 MHz $^{199}Hg\{^1H\}$ NMR spectrum of $[Au_2Hg(P_2phen)_3](PF_6)_2$ in CD_3CN at 25 °C.

The structure of **1** as determined by X-ray diffraction‡ is presented in Fig. 2. The structure contains two trigonally-coordinated Au(I) centers capping a D_3 symmetric cage containing an Hg(0) atom. As can be seen in Fig. 2 the overall geometry of the complex is helical; however the bulk material is racemic as dictated by the centrosymmetric space group. The helicity is reflected in the large P(1)–Au(1)–Au(2)–P(2), P(3)–Au(1)–Au(2)–P(4) and P(5)–Au(1)–Au(2)–P(6) torsion angles of 91.2, 89.1 and 91.9°, respectively. This twisting of the trigonal planes compresses the metallocryptate to accommodate the requisite Au(1)···Au(2) separation of 5.546(1) Å. No attempt was made to resolve **1** into its chiral components.

The Au(1)–Hg(1) and Au(2)–Hg(1) separations are nearly identical at 2.7847(4) and 2.7804(4) Å, respectively. The three-

DOI: 10.1039/b100432h

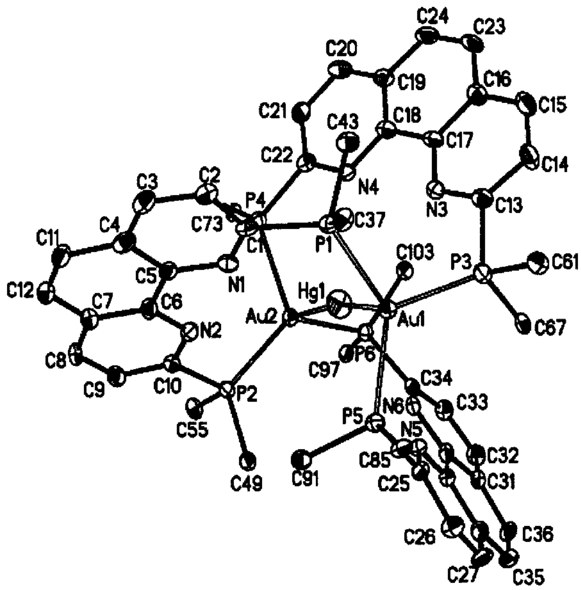


Fig. 2 Thermal ellipsoid plot for the cation of **1**. Hydrogen atoms and phenyl rings are removed for clarity. Selected distances (Å) and angles (°): Au1–Hg1 2.7847(4), Au2–Hg1 2.7807(4), Hg1–N1 3.589(2), Hg1–N2 3.636(2), Hg1–N3 3.374(2), Hg1–N4 3.378(2), Hg1–N5 3.659(2), Hg1–N6 3.604(2); Au1–Hg1–Au2 170.48(1), P1–Au1–P3 113.01(6), P1–Au1–P5 124.49(6), P3–Au1–P5 1217.63(6), P2–Au2–P4 116.01(6), P2–Au2–P6 125.32(5), P4–Au2–P6 113.44(6), P1–Au1–Hg1 98.14(4), P3–Au1–Hg1 94.74(4), P5–Au1–Hg1 98.90(4), P2–Au2–Hg1 98.61(4), P4–Au2–Hg1 95.72(4), P6–Au2–Hg1 98.31(4).

atom linkage is slightly bent with an Au(1)–Hg(1)–Au(2) angle of 170.48(1)°. The two Au atoms are distorted from their respective trigonal coordination planes towards the Hg atom by *ca.* 0.3 Å each. The Hg–N separations range from 3.374(1) to 3.659(1) Å (av. Hg–N 3.540 Å) and are considered non-interacting indicating that the attractive Au–Hg interaction is responsible for maintaining this assembly. The freedom of the Hg atom to move about the cage is reflected by its larger thermal ellipsoid as compared to the Au atoms, a trend noted in other metallocryptands.

The attractive Au–Hg interactions observed here can be rationalized using a simplified molecular orbital approach discussed elsewhere.[10] Although considered formally non-bonding, the metal–metal separations reported here are shorter than the sum of the respective covalent radii (Au = 1.34, Hg = 1.49 Å) indicating a significant attraction between these closed-shell metals. Similar associations with other closed-shell metal ions have been observed in other metallocryptates[9] and in the related trigonally coordinated Pt(0) and Pd(0) phosphine complexes.[14]

The Hg–Au separations described here are shorter than those found in $[Pt(AuPPh_3)_8(Hg)_2]^{4+}$ [3.0070(5) and 3.0011(5) Å][15] and those found in $[(PPh_3)Pt(AuPPh_3)_6(HgNO_3)](NO_3)$ [2.945(3)–3.636(2) Å].[16] Interestingly, in the former complex the Hg is added as Hg(II) while the latter complex is formed by the addition of Hg(0) to $[(PPh_3)Pt(AuPPh_3)_6](NO_3)$. However, to the best of our knowledge there are no reports of a genuine Hg(0) atom coordinating to two Au(I) centers in a linear fashion.

The electronic absorption spectrum (CH_2Cl_2) of **1** shows absorptions attributable to ligand π–π^* transitions between 230 and 280 nm, a broad, unresolved band centered *ca.* 360 nm, and a low energy absorption at 390 nm which may be attributed to the $M_{d\sigma^*} \rightarrow M_{p\sigma^*}$ transition. Compound **1** is weakly emissive, and excitation into the low energy manifold produces an emission band centered at 580 nm. A similar, yet significantly more intense emission is observed in the isoelectronic Tl(I) containing species $[Au_2Tl(P_2phen)_3]^{3+}$ which was assigned to a metal-centered phosphorescence process. Unlike $[Au_2Tl(P_2phen)_3]^{3+}$ compound **1** exhibits an electrochemical oxidation (CH_2Cl_2, irreversible) at *ca.* 1.25 V *vs.* Ag/AgCl. No reversible reductions were observed out to the solvent limit.

The successful encapsulation of Hg(0) by the gold-based metallocryptand further demonstrates the applicability of these inorganic cage complexes as effective probes of closed-shell metal–metal interactions. This methodology may be applied to other d^{10}-based metallocryptands including Pd(0) and Pt(0) where similar metal–metal interactions are expected. Further, by careful ligand manipulation it may be possible to induce a stronger coordination environment around the encapsulated Hg(0) atom. We are actively pursuing these species.

Acknowledgment is made to the National Science Foundation (CHE-9624281) and to the Donors of The Petroleum Research Fund, administered by the American Chemical Society for their generous financial support of this research.

Notes and references

† *Preparation*: $[Au_2Hg(P_2phen)_3](PF_6)_2$ **1**: a 25 mL Erlenmeyer flask was charged with 0.0308 g (5.61 mmol) of 2,9-bis(diphenylphosphino)-1,10-phenanthroline (P_2phen) and 0.100 g (5.61 mmol) of $[Au_2(P_2phen)_2](PF_6)_2$ dissolved in 8 mL of MeCN. To the pale yellow solution was added an excess amount of elemental mercury. This mixture was placed in an ultrasonic cleaner for *ca.* 5 min producing a lemon-yellow solution. The solution was decanted away from excess mercury and filtered through a short pad of Celite. Precipitation with Et_2O afforded a lemon-yellow solid. Yield: (63%).

$C_{108}H_{78}N_6Au_2F_{12}HgP_8{\cdot}2CH_3CN$. Calc. C, 51.38; H, 3.18; N, 3.81. Found: C, 51.22; H, 3.43; N, 3.83%. ^1H NMR (300 MHz, CD_3CN, 25 °C): δ 8.330 (d, J 8.0 Hz), 8.055 (s), 7.526 (d, J 8.42 Hz), 7.501 (m), 7.413 (m), 7.135 (m), 6.740 (m), 6.254 (m), 5.809 (m); $^{31}P\{^1H\}$ (121 MHz, CD_3CN, 25 °C): δ 34.78 [s br (d, $^2J_{HgP}$ 48 Hz)]; $^{199}Hg\{^1H\}$ (89.312 MHz, CD_3CN, 25 °C): δ −1199.8 (hept, $^2J_{PHg}$ 48 Hz)

‡ *Crystal data*: $C_{112}H_{78}Au_2F_{12}HgN_8P_8$, **1**$\cdot 2CH_3CN$ M = 2606.11, monoclinic, space group $P2_1/n$, a = 17.6778(5), b = 29.5895(9), c = 19.4103(6), β = 91.686(1) Å, V = 10148.7(5) Å^3, T = 135 K, Z = 4, μ(Mo-Kα) = 4.595 mm^{-1}, 99 405 reflections measured, 23 285 unique (R_{int} = 0.0452) were used in all calculations. The final $R1$ (all data) was 0.0819 and $wR2$ (all data) was 0.1097 [$R1$ = 0.0487 ($I > 2\sigma I$)]. Single crystals of $[Au_2Hg(P_2phen)_3](PF_6)_2{\cdot}2CH_3CN$ were grown by slow diffusion of diethyl ether into an acetonitrile solution of the complex. A suitable crystal was mounted in inert oil in the N_2 cold stream of a Bruker SMART diffractometer. The data (2.68 < 2θ < 55.00°) were corrected for absorption using SADABS, and the structure was solved by direct methods and refined by full-matrix least squares. CCDC 156335. See http://www.rsc.org/suppdata/cc/b1/b100432h/ for crystallographic data in .cif or other electronic format.

1 L. H. Gade, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 24 and references therein.
2 L. H. Gade, B. F. G. Johnson, J. Lewis, G. Conole and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1992, 3249.
3 Y. Yamamoto, H. Yamazaki and T. Sakurai, *J. Am. Chem. Soc.*, 1982, **104**, 2329.
4 A. D. Burrows and D. M. Mingos, *Coord. Chem. Rev.*, 1996, **154**, 19.
5 G. Schoettel, J. J. Vittal and R. J. Puddephatt, *J. Am. Chem. Soc.*, 1990, **112**, 6400.
6 A. Albinati, A. Moor, P. S. Pregosin and L. M. Venanzi, *J. Am. Chem. Soc.*, 1982, **104**, 7672.
7 L. Hao, J. J. Vittal and R. J. Puddephatt, *Organometallics*, 1996, **15**, 3115.
8 L. Hao, J. J. Vittal and R. J. Puddephatt, *Inorg. Chem.*, 1996, **35**, 269.
9 V. J. Catalano, B. L. Bennett, R. Yson and B. C. Noll, *J. Am. Chem. Soc.*, 2000, **122**, 10 056.
10 V. J. Catalano, B. L. Bennett and B. C. Noll, *Chem. Commun.*, 2000, 1413.
11 V. J. Catalano, B. L. Bennett, H. M. Kar and B. C. Noll, *J. Am. Chem. Soc.*, 1999, **121**, 10 235.
12 R. J. Gillespie, R. Granger, K. R. Morgan and G. J. Schrobilgen, *Inorg. Chem.*, 1984, **23**, 887.
13 B. Wrackmeyer and R. Contreras, in *Annual Reports on NMR Spectroscopy*, ed. G. A. Webb, Academic Press, London, 1992, vol. 24, pp. 267–329.
14 V. J. Catalano, B. L. Bennett, S. Muratidis and B. C. Noll, *J. Am. Chem. Soc.*, 2001, **123**, 173.
15 J. J. Bour, W. v. d. Berg, P. P. J. Schlebos, R. P. F. Kanter, M. F. J. Schoondergang, W. P. Bosman, J. M. M. Smits, P. T. Beurskens, J. J. Steggerda and P. van der Sluis, *Inorg. Chem.*, 1990, **29**, 2971.
16 R. A. T. Gould and L. H. Pignolet, *Inorg. Chem.*, 1994, **33**, 40.