

Gold(I) Pyrazolate Clusters: The Structure and Luminescence of the Tetranuclear, Base-Stabilized [(dppm)₂Au₄(3,5-Ph₂Pz)₂](NO₃)₂ · H₂O

Ahmed A. Mohamed,¹ José M. López-de-Luzuriaga,² and John P. Fackler, Jr.^{1,3}

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The tetranuclear Au(I) pyrazolate complex, [(dppm)₂Au₄(3,5-Ph₂Pz)₂](NO₃)₂ · H₂O, **1**, has been synthesized and structurally characterized. It is the first tetranuclear pyrazolate of Au(I) to have been found, although the trinuclear pyrazolates of Au(I) are well known. Complex **1** exhibits luminescence at 77 K when excited at 333 nm with an emission maximum at 454 nm. The emission has been assigned to ligand to metal charge transfer, LMCT, based upon the vibronic structure that is observed. The complex crystallizes in the monoclinic space group $P2_1/c$, with $a = 19.33(3)$ Å, $b = 20.26(3)$ Å, $c = 19.80(3)$ Å, $\beta = 106.74(2)^\circ$, $V = 7425(17)$ Å³, $Z = 8$, and $R = 0.058$. The Au···Au distances are Au(1)···Au(4) = 3.185(3) Å, Au(1)···Au(2) = 3.230(3) Å, Au(2)···Au(3) = 3.079(3) Å, and Au(3)···Au(4) = 3.280(3) Å.

KEY WORDS: Tetranuclear Au(I) pyrazolate; base-stabilized cluster; aurophilicity; luminescence.

INTRODUCTION

The use of small molecular gold clusters as catalyst precursors for CO and olefin oxidation [1] has prompted renewed interest in gold cluster syntheses. Few Au(I) clusters with hard Lewis base ligands are known. Base-stabilized nitrogen clusters have been reported by Schmidbaur *et al.* [2], such as $[L(PPh_3Au)_4]^{2+}$, $L = 8$ -quinolinaminato(2-) [2a] and $[Au_2N$

¹ Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012, U.S.A.

² Departamento de Química, Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de la Rioja, Madre de Dios 51, E-26006 Logroño, Spain.

³ To whom correspondence should be addressed. E-mail: fackler@mail.chem.tamu.edu

(SiMe₃)(PEt₃)₂]BF₄ [2b]. The majority of reported base stabilized nitrogen ligand compounds contain a Au(I) center coordinated to a tertiary phosphine ligand while the nitrogen donor ligand typically is one in which the N atom is part of an aromatic system [2a, 3–5].

Typically pyrazolate clusters of group 11 elements are trinuclear. Previous work in our laboratory [6] has led to the structural characterization of the homogenous series $[M(\mu\text{-}3,5\text{-Ph}_2\text{Pz})]_3$, $M = \text{Cu(I), Ag(I), Au(I)}$. The hexanuclear gold complex $[\text{Au}(\mu\text{-}3,5\text{-Ph}_2\text{Pz})]_6$ also was obtained, although in poor yield [7]. The chemical oxidation of the trinuclear gold(I) pyrazolate by $\text{PhI}\cdot\text{Cl}_2$ forms the mixed valence $\text{Au}^{\text{I}}\text{Au}^{\text{III}}$ complex, $[\text{AuCl}_2\text{Au}_2(3,5\text{-Ph}_2\text{P}_3)]_3$ [8]. Aqua-regia also oxidizes only one gold atom while chlorinating the pyrazolate ligand. This paper reports the first example of a base stabilized tetranuclear Au(I) pyrazolate cluster.

Structural studies of phosphine stabilized mononuclear Au(I) pyrazolates show that P–Au–N bond is linear [9]. Crossed, aurophilically bonded P–Au–N species also are found [3a, 9]. Reaction of $[\text{dppm}(\text{AuNO}_3)_2]$ with the sodium salt of the pyrazolate ligand produces the $[(\text{dppm})_2\text{Au}_4(3,5\text{-Ph}_2\text{Pz})_2](\text{NO}_3)_2$ cluster that is structurally and spectroscopically described here. This complex exhibits the aurophilic $\text{Au}\cdots\text{Au}$ bonding commonly found in many Au(I) complexes [10]. The complex also exhibits luminescence under UV excitation in the solid state at 77 K.

EXPERIMENTAL

Synthesis

The title cluster was obtained by mixing $[\text{dppm}(\text{AuNO}_3)_2]$ (105 mg, 0.117 mmol) with Na[3,5-diphenylpyrazolate] (28 mg, 0.117 mmol) in 20 ml THF. The reaction mixture was stirred for 3 h and the NaNO₃ produced was filtered off over a Celite 545 bed. The filtrate was concentrated under reduced pressure to 3 ml and ether was added to form a white precipitate. Fine colorless crystals (108 mg, yield 86%) were obtained by slow diffusion of ether into THF solution of the title complex. *Anal.* Calc'd. for $[(\text{dppm})_2\text{Au}_4(3,5\text{-Ph}_2\text{Pz})_2](\text{NO}_3)_2\cdot\text{H}_2\text{O}$, C₈₀H₆₈Au₄N₆P₄O₇: C, 42.65; H, 3.36. Found: C, 42.31; H, 2.97. ³¹P{¹H}NMR: 31 ppm. (The H analysis is low and the C analysis high presumably due to water loss in transport.)

Structure Determination

Data were collected using a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with a LT-2 low-temperature

apparatus operating at 213 K. A suitable hydrocarbon coated crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3° per frame for 60 seconds, such that a hemisphere was collected. The first 50 frames were recollected at the end of data collection as a monitor for decay. The crystal used for the diffraction study showed no decomposition during data collection. Cell parameters were retrieved using SMART [11] software and refined using SAINT [12] on all observed reflections. The esd's (Table I) were based on the initial frames and were not recalculated from the total data. Consequently they are somewhat high. Data reduction was performed using SAINT software which corrects for L_p and decay. Absorption corrections were applied using SADABS [13]. The structure was solved by direct methods using SHELXS-97 [14] and refined by least squares on F^2 , with SHELXL-97 incorporated in SHELXTL-PC V 5.03 [15]. The structure was determined in the space group $P2_1/c$ by analysis of systematic absences. Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. The crystallographic details are given in Table I. Selected bond distances and angles are presented in Table II.

Table I. Crystal Data and Structure Refinement for
 $[(\text{dppm})_2\text{Au}_4(3,5\text{-Ph}_2\text{Pz})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$

Empirical formula	$\text{C}_{80}\text{H}_{68}\text{Au}_4\text{N}_6\text{P}_4\text{O}_7$
Formula weight	2137.19
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 19.33(3)$ Å $b = 20.26(3)$ Å $c = 19.80(3)$ Å $\beta = 106.74(2)$ deg.
Volume, Z	$7425(17)$ Å ³ , 8
Density (calculated)	1.950 g/cm ⁻³
Crystal size	$0.05 \times 0.15 \times 0.15$ mm
Theta range for data collection	1.10 to 28.39°
Limiting indices	$-25 \leq h \leq 25$, $-15 \leq k \leq 26$, $-25 \leq l \leq 26$
Reflections collected	17941
Independent reflections	10987
Data/restraints/parameters	10987/0/511
Goodness-of-fit on F^2	0.905
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0523$, $wR2 = 0.1353$
R indices (all data) ^a	$R1 = 0.1032$, $wR2 = 0.1684$

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [wF_o^4] \}^{1/2}$.

Table II. Selected Bond Distances (Å) and Angles (°) for [(dppm)₂Au₄(3,5-Ph₂Pz)₂](NO₃)₂·H₂O

Bond lengths (Å)			
Au(1)···Au(2)	3.230(3)	Au(2)–N(2)	2.050(10)
Au(2)···Au(3)	3.079(3)	Au(2)–P(2)	2.235(4)
Au(3)···Au(4)	3.280(3)	Au(3)–N(3)	2.054(9)
Au(1)···Au(4)	3.185(3)	Au(3)–P(3)	2.238(4)
Au(1)–N(1)	2.050(9)	Au(4)–N(4)	2.048(10)
Au(1)–P(1)	2.233(4)	Au(4)–P(4)	2.231(4)
Bond angles (°)			
Au(1)···Au(4)···Au(3)	82.71(8)	N(3)–Au(3)···Au(2)	93.5(3)
Au(2)···Au(3)···Au(4)	93.99(8)	N(3)–Au(3)···Au(4)	63.0(3)
Au(4)···Au(1)···Au(2)	92.96(6)	N(4)–Au(4)···Au(1)	102.2(3)
Au(3)···Au(2)···Au(1)	85.20(6)	N(4)–Au(4)···Au(3)	61.5(3)
N(1)–Au(1)–P(1)	178.0(3)	P(1)–Au(1)···Au(4)	91.45(10)
N(2)–Au(2)–P(2)	176.3(3)	P(1)–Au(1)···Au(2)	118.89(11)
N(3)–Au(3)–P(3)	175.8(3)	P(2)–Au(2)···Au(3)	87.10(13)
N(4)–Au(4)–P(4)	174.6(3)	P(2)–Au(2)···Au(1)	115.03(9)
N(1)–Au(1)···Au(4)	90.1(3)	P(3)–Au(3)···Au(2)	90.62(12)
N(1)–Au(1)···Au(2)	62.3(3)	P(3)–Au(3)···Au(4)	115.71(11)
N(2)–Au(2)···Au(3)	95.6(3)	P(4)–Au(4)···Au(1)	81.79(9)
N(2)–Au(2)···Au(1)	62.8(3)	P(4)–Au(4)···Au(3)	122.97(11)

Photoluminescence Studies

Emission and excitation spectra were recorded on a SLM AMINCO, Model 8100 spectrofluorometer equipped with a xenon lamp. Spectra were corrected for instrumental response. Solid state low-temperature measurements were made using a cryogenic sample holder of local design. Powder samples were attached to the holder with a mixture of copper powder, Cryogen oil (used for mounting crystals for x-ray structures) and collodion (a ether and alcohol soluble transparent nitrocellulose). The glue was scanned for a baseline subtraction. Liquid nitrogen was used to obtain the 77 K measurements.

RESULTS AND DISCUSSION

Molecular Structure of 1

The tetranuclear Au(I) pyrazolate complex, [(dppm)₂Au₄(3,5-Ph₂Pz)₂](NO₃)₂·H₂O, **1**, crystallizes in the space group *P2*₁/*c*. The molecular structure of the cation of **1** is shown in Fig. 1. The structure

consists of nearly linear P–Au–N coordination with nitrate counter anions well removed from the Au(I). The mean Au–P and Au–N distances are 2.24 and 2.05 Å, respectively, Table II. The Au⋯Au distances are Au(1)⋯Au(4) = 3.185(3) Å, Au(1)⋯Au(2) = 3.230(3) Å, Au(2)⋯Au(3) = 3.079(3) Å and Au(3)⋯Au(4) = 3.280(3) Å, typical of other Au(I)⋯Au(I) interactions [16]. The Au⋯Au distance in [dppm(AuCl)₂], 3.351(2) Å, is slightly longer than the distances found in the title cluster [16c]. The Au(4)⋯Au(1)⋯Au(2), Au(3)⋯Au(2)⋯Au(1), Au(2)⋯Au(3)⋯Au(4) and the Au(1)⋯Au(4)⋯Au(3) angles (deg) are, respectively, 92.96(6), 85.20(6), 93.99(8), and 82.71(8). The P–Au–N angles of 176° (ave.) show a deviation from linearity that is consistent with the Au⋯Au interactions. One Au(I) atom is found 0.5 Å out of the plane of the other three as seen in Fig. 1. The torsion angle for Au(1)Au(2)Au(3)Au(4) is 17.0°.

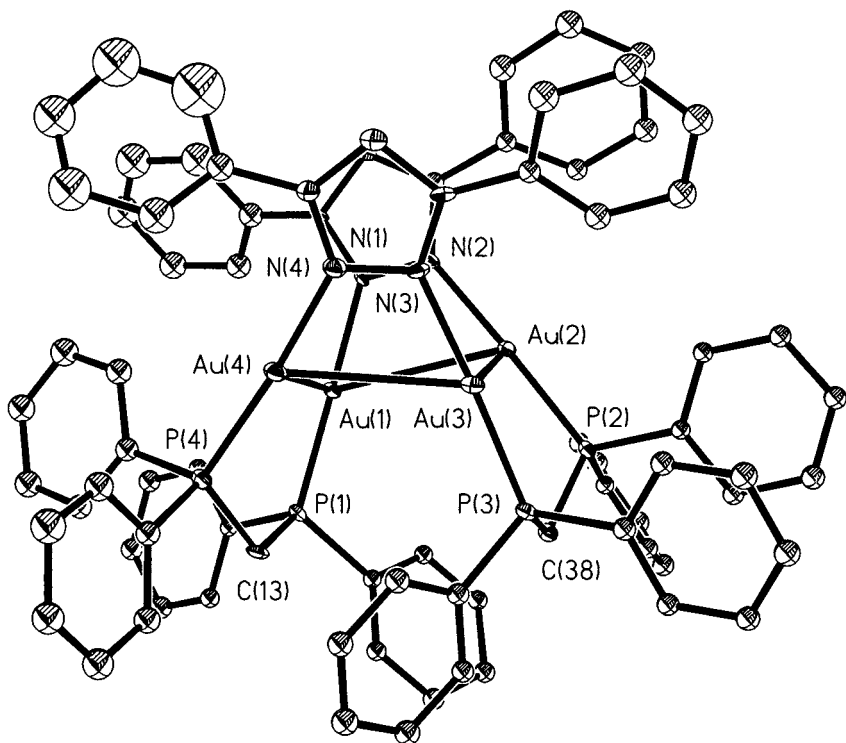


Fig. 1. Thermal ellipsoid probability (50%) plot of [(dppm)₂Au₄(3,5-Ph₂Pz)₂](NO₃)₂·H₂O. Au(1)⋯Au(4) = 3.185(3) Å, Au(1)⋯Au(2) = 3.230(3) Å, Au(2)⋯Au(3) = 3.079(3) Å, and Au(3)⋯Au(4) = 3.280(3) Å.

Table III. Selected Bond Distances (Å) and Angles (°) for Some Tetranuclear Gold Complexes

Complex	Au···Au (Å)av	Au(1)···Au(2)···Au(3) °(av)	X–Au–Y°	Ref.
1 [AuCl(pip)] ₄	3.30	88.3	176.0	16a
2 [Au ₄ (dpmp) ₂ Cl ₂] ²⁺	3.10	90	166.9	17
3 [(PPh ₃) ₄ Au ₄ (SC ₆ H ₄ CH ₃) ₂] ²⁺	3.16	90	174.59	18
4 [(<i>o</i> -tol)P(AuPPh ₃) ₄] ²⁺	2.96		174.62	19
5 HC[Au ₄ (PPh ₃) ₄] ⁺	2.80		172.35	20
6 [(Cy ₃ P)B{Au(PPh ₃) ₄ }] ⁺	2.81	89.67		21
7 [Au(PhNNNPh)] ₄	2.85	89.92	176.0	22
8 [Au ₄ (CH ₃ CS ₂) ₄]	3.01	89.95	167.67	23
9 [L(PPh ₃ Au) ₄] ²⁺	2.98		171.85	2a
10 [(dppm) ₂ Au ₄ (Ph ₂ Pz) ₂] ²⁺	3.19	88.71	176.17	this work

dpmp = bis(diphenylphosphinomethyl)phenylphosphine, L = 8-quinolinaminato(2-).

Table III gives Au···Au distances and the Au···Au···Au and ligand X–Au–Y angles in several reported tetranuclear Au(I) complexes. The Au···Au distances range from 2.80–3.30 Å, typical of aurophilically bonded compounds. In addition there is a tendency to form squares with the Au(1)···Au(2)···Au(3) angles close to 90° [2a, 16a, 17–23]. The X–Au–Y angle is slightly distorted from linearity presumably due to aurophilic interactions. In the title cluster, the Au···Au distance of 3.19 Å probably is influenced by the bridging dppm ligands. It appears that in all of the structures of tetragold species, a short aurophilic bonding supports their stability. In the [L(PPh₃)Au]₄²⁺ species reported by Schmidbaur the gold atoms are in a rhomboidal Au₄ arrangement, with three gold atoms μ₃-bridged by the amido nitrogen atoms and the fourth ligated to the pyridine nitrogen center.

The structure of the title compound shows that the four gold atoms are located at the corner of a distorted square with the pyrazolates and the dppm ligands bridged above and below the near plane of the four Au(I) atoms. The Au(I) atoms bridged by dppm show shorter Au···Au distances than those bridged by the pyrazolate ligands, Fig. 1 and Table II. These bridging phosphine ligands presumably stabilize the aurophilic d¹⁰–d¹⁰ interactions [24].

The molecular structure of the protonated ligand, HPh₂Pz, is tetranuclear [3,5-Ph₂Pz]₄, with an arrangement similar to the cluster cation reported here. The pyrazole units of the tetramer are H-bonded to each other. The distances between N atoms bridged by an H atom average 2.86 Å and the N–H–N angle is 176°, which is similar to the P–Au–N in the

title cluster. Since Au(I) is isolobal to H^+ , these structural similarities are to be expected between the two tetranuclear entities.

Similar structural arrangements to those found in the title structure have been found in the tetrameric 1,3-diphenyltriazenidogold(I) complex, $[Au(PhNNPh)]_4$ and $[Au_4(CH_3CS_2)_4]$, which have mean Au...Au distances of 2.85 and 3.01 Å, respectively (Table III) [22, 23].

The trapezoidal Au–N–N–Au structure in the title complex has been compared with the trinuclear species, $[Au(3,5-Ph_2Pz)]_3$. The former has a N–N–Au = 117.05°; while the later has an angle of 120.20°. The smaller angle at N in the title complex, compared to the trinuclear structure, probably is caused by the dppm ligand which brings the gold atoms into close proximity.

Photoluminescence Studies of 1

Complex 1 is visibly luminescent in the solid state at temperatures below $-20^\circ C$. Excitation at 333 nm produces an emission maxima located at 454 nm. Figure 2 presents the excitation and emission spectra of the complex at 77 K. A phosphorescent emission originating from a metal centered (MC) state is common in polynuclear Au(I) phosphine derivatives. The Stokes shift between the excitation and emission bands suggests a distortion in the excited state which is consistent with strengthened Au(I)–Au(I) bonding as has been observed in the vibrational spectrum of a dinuclear Au(I) dppm complex [25]. The ligands themselves do not show visible emission under these experimental conditions and are not considered responsible for the emission. There is a vibronic structure in the emission spectrum with a spacing between the local maxima of the emission bands of 1454 cm^{-1} . This structure probably corresponds to the stretching $\nu(C=N)$ or $\nu(N=N)$ vibrational modes of the pyrazolate ligand and implicates the pyrazolate ligand in the emission process. Based upon these observations, the emission appears to be ligand to metal charge transfer, LMCT, involving the pi electronic ground state of the ligand.

SYNOPSIS

Gold(I) Pyrazolate Clusters: The Structure and Luminescence of the Tetranuclear, Base-Stabilized $[(dppm)_2Au_4(3,5-Ph_2Pz)_2](NO_3)_2 \cdot H_2O$

The tetranuclear gold(I) complex, $[(dppm)_2Au_4(3,5-Ph_2Pz)_2](NO_3)_2 \cdot H_2O$, has been synthesized and structurally characterized. The complex exhibits luminescence at 77 K with an emission maximum at 454 nm when

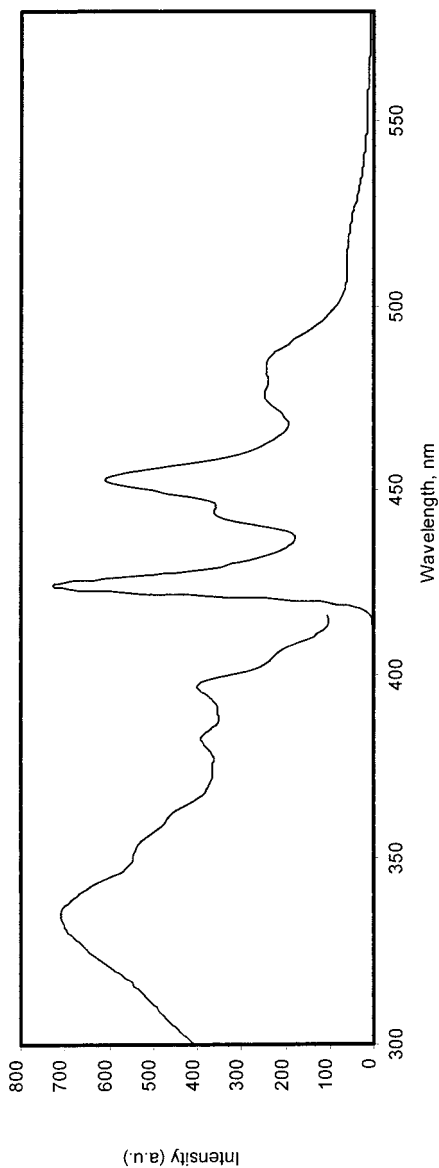
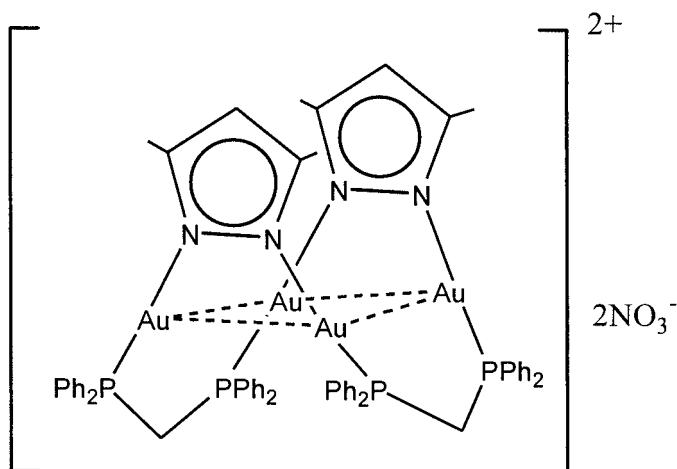


Fig. 2. Solid state excitation and emission spectra of $[(dppm)_2Au_4(3,5-Ph_2Pz)_2](NO_3)_2$ at 77 K. Excitation wavelength = 333 nm.

excited at 333 nm. The emission shows vibronic structure and appears to be associated with a ligand to metal charge transfer process.



SUPPLEMENTAL MATERIALS AVAILABLE

Crystallographic data for the structural analysis of **1** as been deposited with the Cambridge Crystallographic Data Center, CCDC, No. 190228. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, United Kingdom, by quoting the publication citation and the deposition number. [Fax: (int. code) +44 (1223)336-033, E-mail: deposit@ccdc.cam.ac.uk, URL: <http://www.ccdc.cam.ac.uk>]

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