Supporting Material

A hexanuclear gold(I) metallatriangle derived from a chiral dithiophosphonate: synthesis, structure, luminescence and oxidative bromination reactivity

Michael N. Pillay,[†] Bernard Omondi,[†] Richard J. Staples,[‡] and Werner E. van Zyl*,[†]
Email: vanzylw@ukzn.ac.za

[†]School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban, 4000, South Africa.
[‡]Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322, United States

General Instrumentation

Nuclear Magnetic resonance: All NMR was carried out at ambient temperature (298 K). Solution NMR experiments was carried out on a Bruker 400 MHz spectrometer. ^{1}H spectra, expressed in parts per million (ppm), are referenced internally to residual proton impurity in the deuterated solvents (δ_H) multiplicity(**s** = singlet; **d** = doublet; **dd =** doublet of doublets; **t** = triplet; and **m**= multiplet). ^{31}P nuclei chemical shifts were referenced relative to an 85% H_3PO_4 in D_2O external standard solution. Solid state ^{31}P NMR spectra were obtained on a Bruker 600MHz operating at room temperature with a magic angle spinning (MAS) probe.

Luminescence: Luminescence data were collected on a Perkin Elmer LS55 Fluorescence Spectrometer, fitted with a front surface accessory.

Crystallography: Data for both **1** and **2** were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 173 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO[S1] where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software[S2] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[S3] which corrects for Lp. Scaling and absorption corrections were applied using SADABS[S4] multi-scan technique, supplied by George Sheldrick.

The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL- 97, which are incorporated in SHELXTL-PC V 6.10.[S5]

Complex **1** had one CH_2Cl_2 solvent molecule, but a void was also observed within the crystal structure. There is a possibility that the crystal lost some solvent leaving the void. The crystal remained intact in air for over 24 hours. Other solvents that were used for crystallization were CH_2Cl_2, hexane, and THF. There were no large residual density peaks in the structure.

References

S1. COSMO V1.61, *Software for the CCD Detector Systems for Determining Data Collection Parameters.* Bruker Analytical X-ray Systems, Madison, WI (2009).

S2. APEX2 V2010.11-3. Software *for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (2010).

S3. SAINT V 7.68A Software *for the Integration of CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2010).

S4. SADABS V2.008/2 Program for absorption corrections using Bruker-AXS CCD based on the method of Robert Blessing; Blessing, R.H. Acta Cryst. A51, 1995, 33-38.

S5. Sheldrick, G.M. "A short history of SHELX". *Acta Cryst*. **A64**, 2008, 112-122.

Preparation of Ligand and Complexes 1 and 2.

All syntheses were performed utilizing standard Schlenk techniques under an atmosphere of nitrogen.

Synthesis of $(NH_4)_2[(S_2P-1,4-C_6H_4OEt)_2(trans-1,2-O,O'-C_6H_{10})]$.

A Schlenk flask was charged with $(4-C_6H_4OEtP(S)S)_2$ (1.5 g, 3.48 mmol) and placed under vacuum for 30 minutes. The solid was heated to 70 °C, $trans$-1,2-$C_6H_{10}(OH)_2$ (1.5 g, 3.48 mmol) and toluene (2 mL) was added. The temperature was maintained at 70 °C for 60 minutes, until dissolution of all the solids had been observed. The clear residue was cooled to room temperature, before being placed in an ice bath for 10 minutes. Anhydrous NH_3 gas was bubbled

through the residue with vigorous agitation, which caused the immediate precipitation of a white salt. Yield 1.986 g (98%); M.p. 88°C; ^{1}H-NMR (CDCl$_3$, 298 K) ppm: 1.39(m,2H), 1.41 (6H, t, J=6.98 Hz), 1.63 (2H, m), 1.78 (2H, m), 2.18 (2H, d, J=12.61 Hz), 4.06 (q, 4H, J=6.98 Hz), 4.92 (m,2H), 6.93 (dd, 4H, J=3.84, 8.84 Hz), 7.88 (dd, 4H, J=8.82, 13.95 Hz); ^{31}P NMR (CDCl$_3$, 298 K) $\delta = 105.3$ (s, 2P).

Synthesis of 1.

A Schlenk flask was charged with (NH$_4$)$_2$[(S$_2$P-1,4-C$_6$H$_4$OEt)$_2$(*trans*-1,2-O,O'-C$_6$H$_{10}$)] (400mg, 0.687 mmol) and dry tetrahydrofuran (40 mL). To the clear solution AuCl(tht) (440 mg, 1.374 mmol) (tht=tetrahydrothiophene) was added and the reaction stirred for 30 min, resulting in the formation of a yellow solution. The solvent was removed in *vacuo,* followed by extraction with 50 mL of dichloromethane. The extract was filtered through a composite of Celite/anhydrous MgSO$_4$. The volume of the filtrate was reduced in *vacuo*. A yellow powder was consolidated and washed with diethyl ether (2 x 5 mL). Yield 580 mg (90 %) of yellow powder soluble in chlorinated organic solvents. Single crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane layered onto a concentrated dichloromethane solution of **1**. M.p. 167°C; Solution NMR showed signs of reactivity towards the solvent. Solid state MAS ^{31}P NMR spectrum shown in Figure S1.

Synthesis of 2.

A Schlenk flask was charged with **1** (427mg, 0.15mmol), and dichloromethane (20 mL). To the solution bromine (15 μL, 0.30 mmol) was added and stirred for 30 min. The solvent was removed in *vacuo*. A red crystalline powder was obtained. Yield 567mg (86.4%). Single crystals suitable for X-ray diffraction studies were grown by slow diffusion of hexane layered onto a concentrated dichloromethane solution of **2**. M.p. 157°C; ^{1}H-NMR (CDCl$_3$, 298 K) ppm: 1.09-1.91(10H), 4.08(q, 4H, $J = 6.88$ Hz), 4.91(m, 2H), 7.04(dd, 4H, $J = 3.82$, 8.92 Hz), 7.81(dd, 4H, $J = 8.91$, 13.97 Hz); Solution ^{31}P NMR spectrum shown in Figure S2.
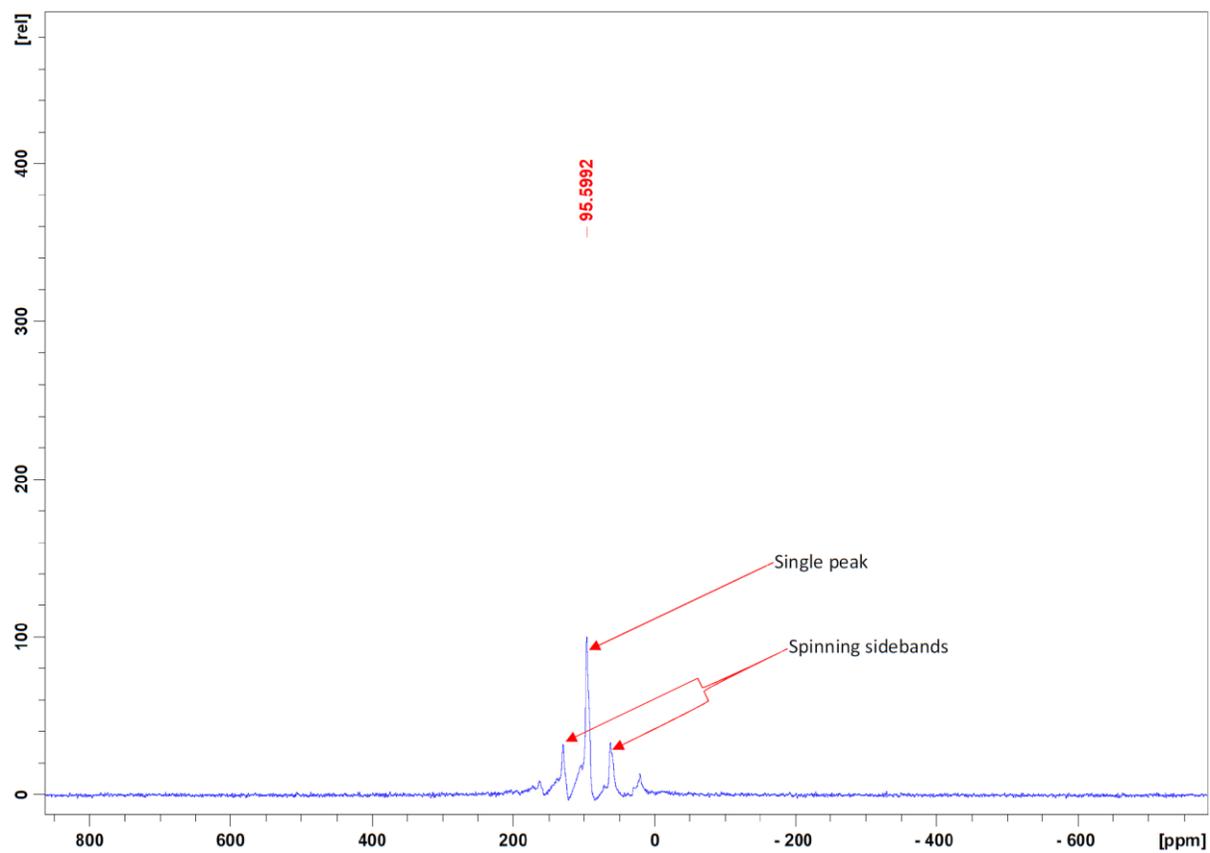
Figure S1. Solid-state ^{31}P NMR spectrum of **1** collected at 8 kHz, a few spinning sidebands are shown. The sidebands were distinguished from the real peaks by varying the spin rate of the rotor in three consecutive experiments with the same sample.
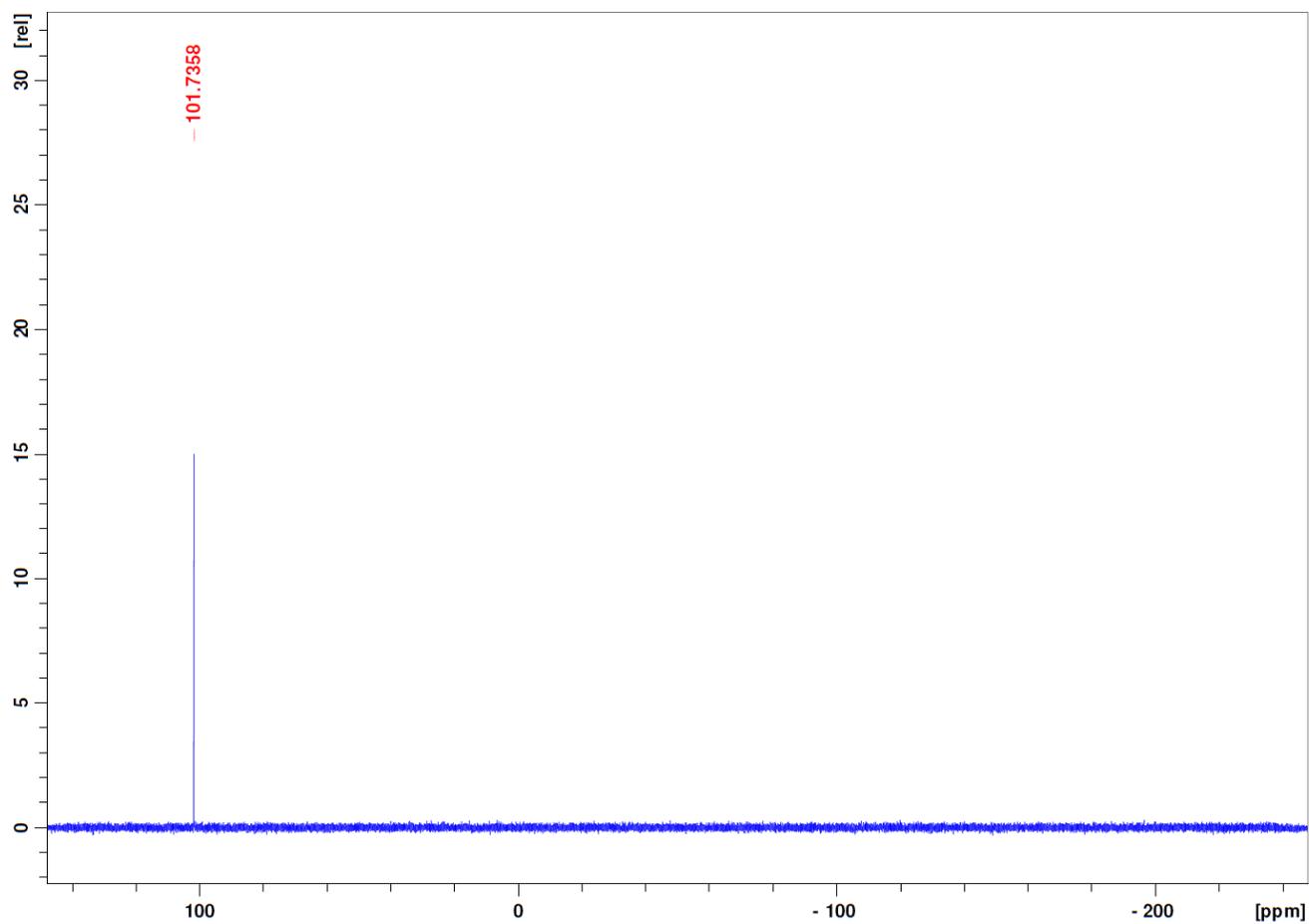
Figure S2. Solution ^{31}P NMR spectrum of **2**.

Table S1. Crystallographic and refinement data for complex **1**·CH_2Cl_2

Empirical formula	$C_{67} H_{86} Au_6 Cl_2 O_{12} P_6 S_{12}$
Formula weight	2906.60
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Tetragonal
Space group	I 41/a
Unit cell dimensions	a = 26.7928(18) Å α= 90°.
	b = 26.7928(18) Å β= 90°.
	c = 54.090(4) Å γ = 90°.
Volume	38828(5) $Å^3$
Z	16
Density (calculated)	1.989 Mg/m^3
Absorption coefficient	9.495 mm^{-1}
F(000)	21984
Crystal size	0.24 x 0.16 x 0.09 mm^3
Theta range for data collection	1.70 to 25.40°.
Index ranges	-31<=h<=32, -32<=k<=32, -64<=l<=65
Reflections collected	143138
Independent reflections	17883 [R(int) = 0.0664]
Completeness to theta = 25.40°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6746 and 0.3954
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	17883 / 0 / 952
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0357, wR2 = 0.0911
R indices (all data)	R1 = 0.0590, wR2 = 0.1045
Largest diff. peak and hole	2.690 and -1.638 e.$Å^{-3}$

Table S2. Crystallographic and refinement data for complex **2.**

Empirical formula	$C_{22} H_{28} Au_2 Br_4 O_4 P_2 S_4$
Formula weight	1260.20
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/c
Unit cell dimensions	a = 11.2132(8) Å α= 90°.
	b = 15.3143(11) Å β= 92.7980(10)°.
	c = 19.9458(15) Å γ = 90°.
Volume	3421.1(4) Å^3
Z	4
Density (calculated)	2.447 Mg/m^3
Absorption coefficient	13.604 mm^{-1}
F(000)	2336
Crystal size	0.12 x 0.12 x 0.07 mm^3
Theta range for data collection	1.68 to 25.35°.
Index ranges	-13<=h<=13, -18<=k<=18, -24<=l<=23
Reflections collected	27477
Independent reflections	6250 [R(int) = 0.0425]
Completeness to theta = 25.00°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4671 and 0.2833
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6250 / 0 / 345
Goodness-of-fit on F^2	1.019

Final R indices [I>2sigma(I)]	R1 = 0.0299, wR2 = 0.0617
R indices (all data)	R1 = 0.0469, wR2 = 0.0673
Largest diff. peak and hole	1.007 and -0.710 e.Å^{-3}