

INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN
CHEMISTRY AND PHARMACEUTICAL SCIENCES

(p-ISSN: 2348-5213; e-ISSN: 2348-5221)

www.ijrcrcps.com

Codon: IJCROO(USA)

Volume 3, Issue 7 - 2016

Research Article

SOI: <http://s-o-i.org/1.15/ijrcrcps-2016-3-7-5>

Gold (III)-diacetyl-1,3,5-Triaza-7-phosphaadamantane (DAPTA)- arylazo-imidazole complexes : Synthesis and Spectroscopic study.

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Abstract

Reaction of $[\text{Au}(\text{DAPTA})(\text{Cl})_3]$ with RaaiR' in CH_2Cl_2 medium following ligand addition leads to $[\text{Au}(\text{DAPTA})(\text{RaaiR}')(\text{Cl})]$ [DAPTA = diacetyl-1,3,5-Triaza-7-phosphaadamantane, $\text{RaaiR}' = p\text{-R-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{-NN-1-R}'$, (1-3), abbreviated as $\text{N,N}'$ -chelator, where N(imidazole) and N(azo) represent N and N' , respectively; R = H (a), Me (b), Cl (c) and $\text{R}' = \text{Me}$ (1), CH_2CH_3 (2), CH_2Ph (3)]. The ^1H NMR spectral measurements in D_2O suggest methylene, $-\text{CH}_2-$, in RaaiEt gives a complex AB type multiplet while in RaaiCH_2Ph it shows AB type quartets. ^{13}C NMR spectrum in D_2O suggest the molecular skeleton. In the $^1\text{H}-^1\text{H}$ COSY spectrum in D_2O as well as contour peaks in the $^1\text{H}-^{13}\text{C}$ HMQC spectrum in D_2O assign the solution structure.

Keywords:

1. Introduction

Due to its utility as a water-soluble ligand and in efforts to explore the unique chemistry of this ligand, Darenberg's group has been active in the investigation of the different facets of PTA [1-9]. Further, PTA has been investigated in many different areas such as photoluminescence of gold(I) phosphine complexes [4-8] and intermolecular hydrogen-metal interactions [9], as well as its use as a precursor to other novel phosphine amine compounds and ligands. One commonly used strategy to impart water-solubility to a given metal complex involves the use of those selected for this study: 1,3,5-triaza-7-phosphaadamantane (PTA); 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1] nonane (DAPTA); monosulfonated triphenylphosphine (TPPMS); disulfonated triphenylphosphine (TPPDS); trisulfonated triphenylphosphine (TPPTS). All five phosphines are soluble in water and have previously been used as ligands possessing solubilizing groups or use of water-soluble ligands. Typical examples of such ligands are

ligands in various metal complexes including some examples of gold(I) and gold(III). In this paper, the reaction of RaaiR' on gold(III) DAPTA derivatives were examined and the products were isolated, $[\text{Au}(\text{DAPTA})(\text{RaaiR}')(\text{Cl})]$. The complexes are well characterised by IR, ^1H NMR, ^{13}C NMR, $^1\text{H}-^1\text{H}$ COSY, $^1\text{H}-^{13}\text{C}$ HMQC NMR spectrometry.

2. Experimental

All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. IR spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, $4000\text{-}200\text{ cm}^{-1}$). The ^1H NMR spectra in CDCl_3 were obtained on a Bruker 500 MHz FT NMR spectrometer using SiMe_4 as internal reference, CFCl_3 .

Preparation of the complexes: [diacetyl-(1,3,5-triaza-7-phosphaadamantane){1-ethyl-2-(p-tolylazo)imidazole} aurate (III)] chloride, [Au(DAPTA)(HaaiEt)](Cl), (2b):

To a CH₂Cl₂ solution (15 cm³) of [Au(DAPTA)Cl₃] (0.945 g, 0.20 mmol), was added a yellow CH₂Cl₂ solution of 1-ethyl-2-(p-tolylazo)imidazole, slowly, dropwise, and the mixture was stirred at 343-353 K for 12 h. Where respectively added the other ligands, HeaaiMe (0.0186 g, 0.1 mmol, 1a), MeaaiMe (0.020 g, 0.1 mmol, 1b), ClaiiMe (0.0220 g, 0.1 mmol, 1c), HaaiEt (0.020 g, 0.1 mmol, 2a), MeaaiEt (0.0214 g, 0.1 mmol, 2b), ClaiiEt (0.0235 g, 0.1 mmol, 2c), HaaiBz (0.0262 g, 0.1 mmol, 3a), MeaaiBz (0.0276 g, 0.1 mmol, 3b), ClaiiBz (0.0297 g, 0.1 mmol, 3c), The orange solution that resulted was concentrated (4 cm³) and kept in a refrigerator overnight (1 h). The addition of hexane to the above red solution gives precipitate which was collected by filtration, washed thoroughly with hexane to remove excess ligand and then dried *in vacuo* over pump overnight. The yield was 0.08 g (70%). All other complexes were prepared similarly as stated above. Analysis for [Au(DAPTA)(HaaiMe)](Cl), (1a), Found: C, 38.8, H, 4.9, N, 15.6, Calcd for [C₂₀H₂₈N₇O₂AuP](Cl), C, 38.3, H, 4.5, N, 15.8; IR(nujol, cm⁻¹), ν(N=N) 1370 ν(C=N) 1590, ν(DAPTA COCH₃) 1670, 780, ³¹P{H}NMR, ppm, 45.29; ¹H NMR, ppm, 8.27(d, H(7,11), J = 8Hz), 8.21(d, H(8,10), J=6.5Hz), 1.99(s, H(CH₃),), 7.26(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(MeariMe)](Cl), (1b), Found: C, 39.8, H, 4.7, N, 15.6, Calcd for [C₂₁H₃₀N₇O₂AuP](Cl), C, 39.3, H, 4.5, N, 15.5; IR(nujol, cm⁻¹), ν(N=N) 1370 ν(C=N) 1599, ν(DAPTA COCH₃) 1679, 790, ³¹P{H}NMR, ppm, 45.69; ¹H NMR, ppm, 8.2(d, H(7,11), J = 8Hz), 8.2(d, H(8,10), J=6.5Hz), 1.9(s, N(CH₃),), 7.2(d, H(4), J=6Hz), 7.3(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10), 134(C6); Analysis for [Au(DAPTA)(ClaiiMe)](Cl), (1c), Found: C, 36.8, H, 4.1, N, 15.0, Calcd for [C₂₀H₂₇N₇O₂AuP](Cl), C, 36.3, H, 4.1, N, 15.0; IR(nujol, cm⁻¹), ν(N=N) 1379 ν(C=N) 1590, ν(DAPTA COCH₃) 1670, 790, ³¹P{H}NMR, ppm, 45.29; ¹H NMR, ppm, 8.7(d, H(7,11), J = 8Hz), 8.1(d, H(8,10), J=6.5Hz), 1.9(s, N(CH₃),), 7.2(d, H(4), J=6Hz), 7.3(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(HaaiEt)](Cl), (2a), Found: C, 39.8, H, 4.9, N, 15.6, Calcd for [C₂₁H₃₀N₇O₂AuP](Cl), C, 39.8, H, 4.5, N, 15.8; IR(nujol, cm⁻¹), ν(N=N) 1379 ν(C=N) 1599, ν(DAPTA COCH₃) 1679, 780, ³¹P{H}NMR, ppm, 45.9; ¹H NMR, ppm, 8.7(d, H(7,11), J = 5Hz), 8.2(d, H(8,10), J=6.5Hz), 4.5, 1.9(q,s, J=9Hz, H(Et),), 7.2(d, H(4), J=6Hz), 7.3(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 134.5(C2), 124(C4), 125(C5), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(MeariEt)](Cl), (2b), Found: C, 40.8, H, 4.9,

N, 15.2, Calcd for [C₂₂H₃₂N₇O₂AuP](Cl), C, 40.8, H, 4.5, N, 15.2; IR(nujol, cm⁻¹), ν(N=N) 1379 ν(C=N) 1590, ν(DAPTA COCH₃) 1670, 790, ³¹P{H}NMR, ppm, 45.3; ¹H NMR, ppm, 8.7(d, H(7,11), J = 8Hz), 8.2(d, H(8,10), J=6.5Hz), 4.6, 1.99(q,t, J=8Hz, H(Et),), 7.26(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 134.5(C2), 124(C4), 125.3(C7,11), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(ClaiiEt)](Cl), (2c), Found: C, 37.8, H, 4.3, N, 14.6, Calcd for [C₂₁H₂₉N₇O₂AuP](Cl), C, 37.3, H, 4.5, N, 14.8; IR(nujol, cm⁻¹), ν(N=N) 1378 ν(C=N) 1599, ν(DAPTA COCH₃) 1674, 780, ³¹P{H}NMR, ppm, 45.9; ¹H NMR, ppm, 8.7(d, H(7,11), J = 8Hz), 8.1(d, H(8,10), J=6.5Hz), 4.3, 1.9(q,t, J=6Hz, H(Et),), 7.2(d, H(4), J=6Hz), 7.3(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(HaaiBz)](Cl), (3a), Found: C, 42.8, H, 4.3, N, 13.6, Calcd for [C₂₆H₃₂N₇O₂AuP](Cl), C, 42.3, H, 4.5, N, 13.3; IR(nujol, cm⁻¹), ν(N=N) 1375 ν(C=N) 1598, ν(DAPTA COCH₃) 1671, 780, ³¹P{H}NMR, ppm, 45.29; ¹H NMR, ppm, 8.7(d, H(7,11), J = 8Hz), 8.2(d, H(8,10), J=6.5Hz), 4.9, 7.0-7.2(s, H(Bz),), 7.2(d, H(4), J=6Hz), 7.4(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(MeariBz)](Cl), (3b), Found: C, 43.1, H, 4.3, N, 13.0, Calcd for [C₂₇H₃₄N₇O₂AuP](Cl), C, 43.3, H, 4.5, N, 13.3; IR(nujol, cm⁻¹), ν(N=N) 1375 ν(C=N) 1598, ν(DAPTA COCH₃) 1676, 790, ³¹P{H}NMR, ppm, 45.9; ¹H NMR, ppm, 8.7(d, H(7,11), J = 8Hz), 8.4(d, H(8,10), J=6.5Hz), 4.9, 7.0-7.2(s, H(Bz),), 7.2(d, H(4), J=6Hz), 7.4(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 124(C4), 125(C5), 129.2(C8,10), 134(C6); Analysis for [Au(DAPTA)(ClaiiBz)](Cl), (3c), Found: C, 40.8, H, 4.0, N, 12.6, Calcd for [C₂₆H₃₁N₇O₂AuP](Cl), C, 40.3, H, 4.0, N, 12.7; IR(nujol, cm⁻¹), ν(N=N) 1375 ν(C=N) 1598, ν(DAPTA COCH₃) 1670, 780, ³¹P{H}NMR, ppm, 45.9; ¹H NMR, ppm, 8.7(d, H(7,11), J = 8Hz), 8.9(d, H(8,10), J=6.5Hz), 4.9, 7.0-7.29(s, H(Bz),), 7.2(d, H(4), J=6Hz), 7.4(d, H(5), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, ppm, 124(C4), 125(C5), 125.9(C7,11), 128.2(C8,10), 134(C6).

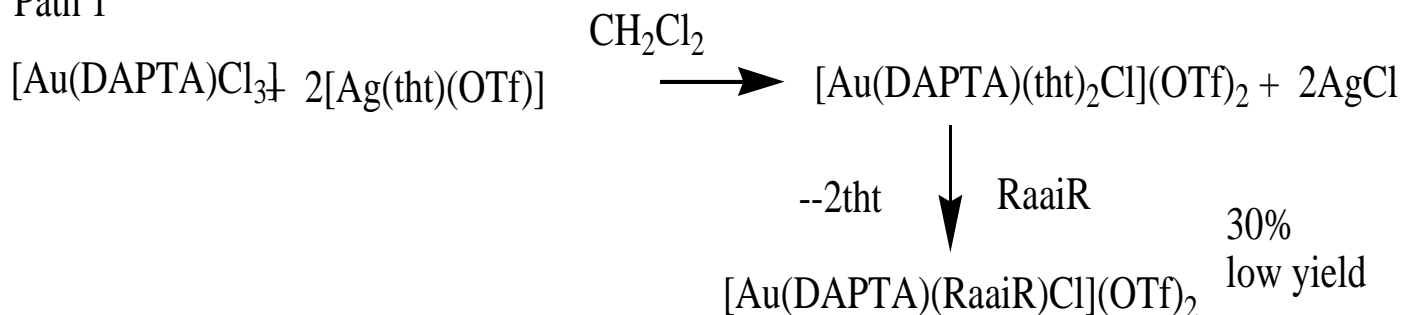
Results and Discussion

The complexes, [Au(DAPTA)(RaaiR')](Cl) [DAPTA = diacetyl-1,3,5-triaza-7-phosphaadamantane, RaaiR' = *p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', (1-3), abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H (a), Me (b), Cl (c) and R' = Me (1), CH₂CH₃ (2), CH₂Ph (3)], were prepared by removing Chloride by silver assisted pathway under stirring at 343-353 K in MeOH solution in poor yield (35-40%). Here the reaction goes through unknown gold-silver cluster formation. Whereas in path I, direct substitution gives high yield (80-85 %). The synthetic routes are shown in *Scheme 1*. The composition of the complexes is supported by microanalytical results.

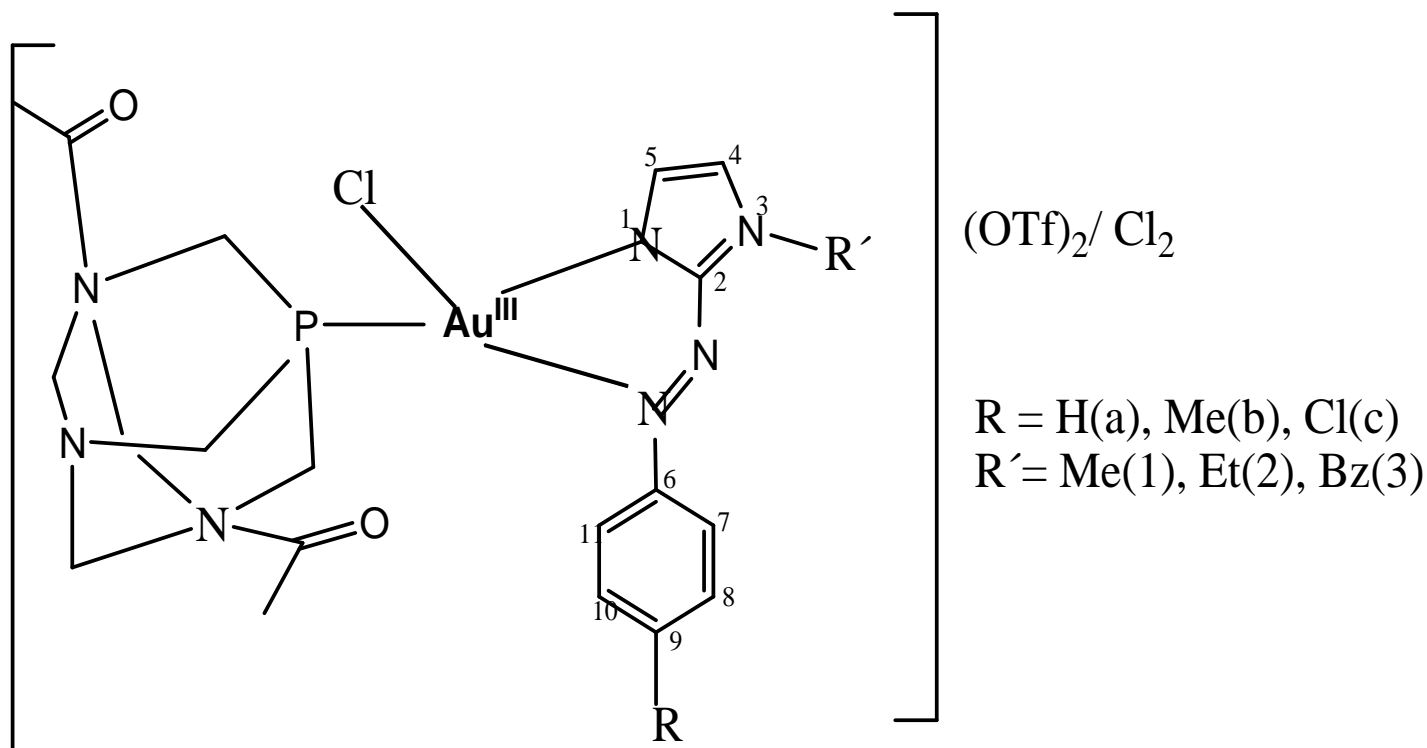
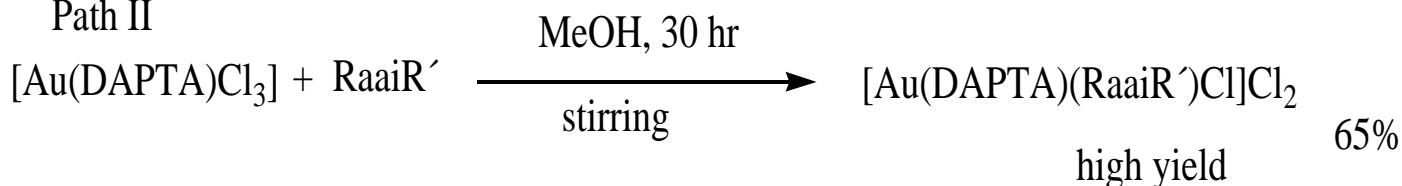
The red orange complexes are not soluble in common organic solvents viz. acetone, acetonitrile, chloroform, dichloromethane but soluble in H₂O, methanol,

ethanol. These are the water soluble golden complexes.

Path 1



Path II



Scheme 1

Spectral study : IR spectra of the complexes, [Au(DAPTA)(RaaiR')](Cl) show a 1:1 correspondence to the spectra of the chloro analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm⁻¹ with concomitant loss of ν(Au-Cl) at 320-340 cm⁻¹. They are assigned to ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm⁻¹, respectively. Other important frequencies are

ν(DAPTA) 780-800 cm⁻¹. Phosphorous NMR, ³¹P{¹H}NMR, gives a concrete idea on the nature of complexes. Due to the presence of azo-imine function, which is pi acidic in nature, stabilises the gold (III) oxidation state giving the value of 45.9. Changing the substitution at R, R' on the ligand there is a slight chemical shift value changes of these complexes.

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How to cite this article:

Prithwiraj Byabartta. (2016). Gold (III)-diacetyl-1,3,5-Triaza-7-phosphaadamantane (DAPTA) - arylazo-imidazole complexes : Synthesis and Spectroscopic study. Int. J. Curr. Res. Chem. Pharm. Sci. 3(7): 22-26.