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

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Abstract

Reaction of $[Au(DAPTA)(CI)_3]$ with RaaiR in CH_2CI_2 medium following ligand addition leads to [Au(DAPTA)(RaaiR')](CI) [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), CI (c) and R' = Me (1), CH₂CH₃ (2), CH₂Ph (3),]. The ¹H NMR spectral measurements in D₂O suggest methylene, $-CH_2-$, in RaaiEt gives a complex AB type multiplet while in RaaiCH₂Ph it shows AB type quartets. ¹³C NMR spectrum in D₂O suggest the molecular skeleton. In the ¹H-¹H COSY spectrum in D₂O as well as contour peaks in the ¹H-¹³C HMQC spectrum in D₂O 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 photoluminecence 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); 3,7diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1] nonane (DAPTA); monosulfonated triphenylphosphine (TPPMS); disulfonated triphenylphosphine (TPPDS); trisulfonated triphenylphosphin (TPPTS). All five phosphines are soluble in water and have previously been used as ligands possessing solubilizing groups or use of watersoluble 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, [Au(DAPTA)(RaaiR[/])](CI)]. The complexes are well characterised by IR, ¹H NMR, ¹³C NMR, ¹H-¹H COSY, ¹H-¹³C 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, 4000-200 cm⁻¹). The ¹H NMR spectra in CDCl₃ were obtained on a Bruker 500 MHz FT NMR spectrometer using SiMe₄ as internal reference, CFCl₃.

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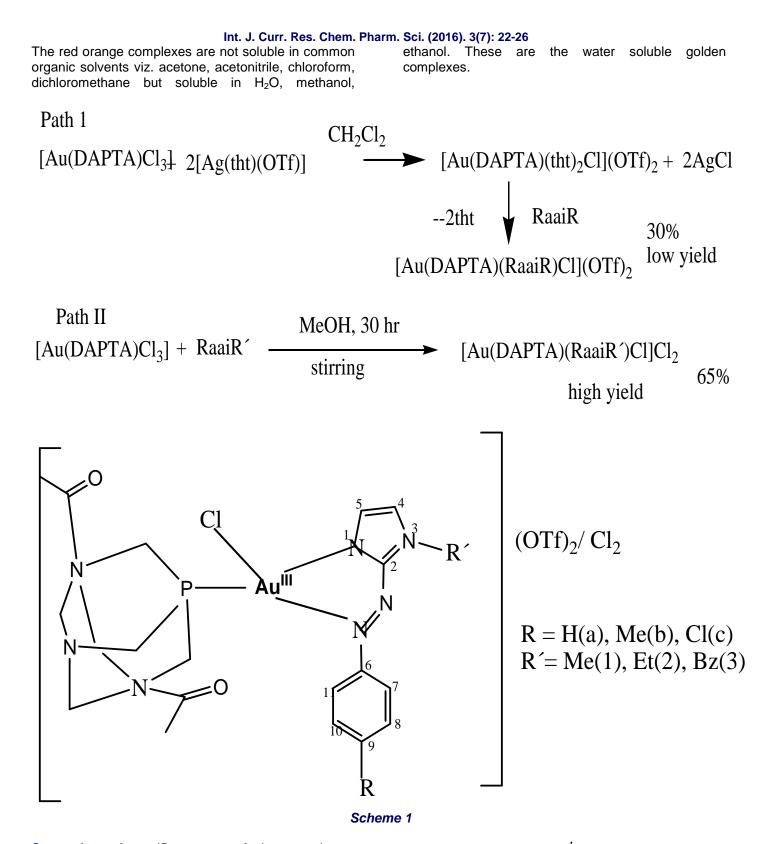
Preparation of the complexes: [diacetyl-(1,3,5-triaza-7-phosphaadamantane){1-ethyl-2-(p-tolylazo) imidazole} aurate (III)] chloride, [Au(DAPTA) (HaaiEt)](CI), (2b):

To a CH_2Cl_2 solution (15 cm³) of [Au(DAPTA)Cl₃] (0.945) g, 0.20 mmol), was added a yellow CH₂Cl₂ solution of 1ethyl-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), ClaaiMe (0.0220 g, 0.1 mmol, 1c), HaaiEt (0.020 g, 0.1 mmol, 2a), MeaaiEt (0.0214 g, 0.1 mmol, 2b), ClaaiEt (0.0235 g, 0.1 mmol, 2c), HaaiBz (0.0262 g, 0.1 mmol, 3a), MeaaiBz (0.0276 g, 0.1 mmol, 3b), ClaaiBz (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), v(N=N), 1370 v(C=N) 1590, v(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)(MeaaiMe)](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}), v(N=N) 1370 v(C=N) 1599, v(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), $^{13}C{}^{1}H{}NMR$, ppm, 134(C2), 124(C4), 125(C5), 125(C7,11), 129(C8,10), 134(C6); Analysis for [Au(DAPTA)(ClaaiMe)](Cl) (1c), Found: C, 36.8, H, 4.1, N, 15.0, Calcd for [C₂₀H₂₇N₇O₂AuPCI](Cl), C, 36.3, H, 4.1, N, 15.0; IR(nujol, cm⁻¹), v(N=N) 1379 v(C=N) 1590, v(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)](CI) (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), v(N=N) 1379 v(C=N) 1599, v(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), 125(C5), 124(C4), 134(C6); 129.2(C8.10). Analysis for [Au(DAPTA)(MeaaiEt)](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}), v(N=N) 1379 v(C=N) 1590, v(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)(ClaaiEt)](Cl), (2c), Found: C, 37.8, H, 4.3, N, 14.6, Calcd for [C₂₁H₂₉N₇PO₂AuCl](Cl), C, 37.3, H, 4.5, N, 14.8; IR(nujol, cm⁻¹), v(N=N) 1378 v(C=N) 1599 v(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=5Hz), 4.5, 4.2(DAPTA), J=6Hz), 7.3(d, H(5), 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}), v(N=N) 1375 v(C=N) 1598 v(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)(MeaaiBz)](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), v(N=N) 1375 v(C=N) 1598 v(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)(ClaaiBz)](Cl) (3c), Found: C, 40.8, H, 4.0, N, 12.6, Calcd for [C₂₆H₃₁N₇O₂AuPCI](Cl), C, 40.3, H, 4.0, N, 12.7; IR(nujol, cm⁻¹), v(N=N) 1375 v(C=N) 1598, v(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), J=5Hz), 4.5, 4.2(DAPTA), ¹³C{¹H}NMR, 7.4(d, H(5), ppm, 124(C4), 125(C5), 125.9(C7,11), 128.2(C8,10), 134(C6).

Results and Discussion

The complexes, [Au(DAPTA)(RaaiR')](CI) [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*), CI (*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.



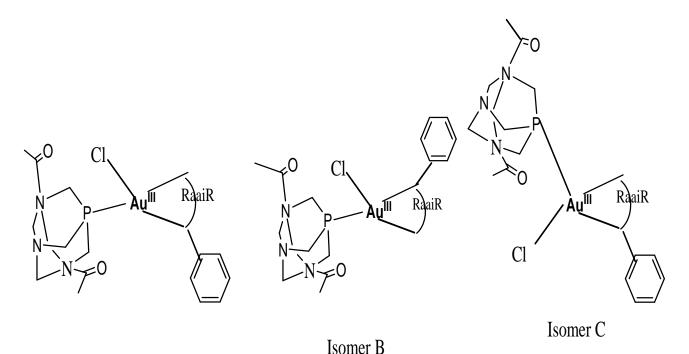
Spectral study : IR spectra of the complexes, $[Au(DAPTA)(RaaiR^{/})](CI)$ show a 1:1 correspondence to the spectra of the chloro analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm⁻¹ with concomitant loss of v(Au-CI) at 320-340 cm⁻¹. They are assigned to v(N=N) and v(C=N)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

v(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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The ¹H NMR spectra of [Au(DAPTA)(RaaiR[/])](CI) (*1-3*) complexes were unambiguously assigned on comparing with [Au(DAPTA)CI] and the free ligand (RaaiR[/]). 1-Me appears as a singlet at 2.0 ppm for [Au(DAPTA)(RaaiMe)]⁺; the methylene protons, 1-CH₂-(CH₃) show AB type quartet (*ca.* 4.4, 4.6 ppm, J = 6-7 Hz) and (1-CH₂)CH₃ gives a triplet at 1.5 ppm (7.0-8.0 Hz) for [Au(DAPTA)(RaaiCH₂CH₃)]⁺. 1-CH₂(Ph) protons appear at AB type quartets (*ca.* 5.5, 5.7 ppm) with geminal coupling constant avg. 8.8 Hz in [Au(DAPTA)(RaaiCH₂Ph)]⁺. Assignment of different

resonant peaks in 13 C (1 H)NMR to respective carbon atoms are done on nine complexes and the data are given on experimental section. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum effected by the magnetic interaction of two bulky phenyl rings environment and electron delocalization on the =N-CC=N- and =N-CC=CC-. The COSY spectrum reveals the 1 H- 1 H coupling interactions in the molecule.



Isomer A

The protons that are decoupled from the adjacent ones due to the lack of α -protons will show no coorelation in the spectrum. Extending horizontal and vertical lines from δ = 8.3 ppm [C(8)H] and 8.6 ppm [C(10)H] encounter cross peaks at δ = 7.12 ppm and 7.23 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The ¹H-¹³C heteronuclear multiplequantum coherence (HMQC) spectrum provides information regarding the interaction between the protons and the carbon atoms to which they are directly attached. The peaks observed at δ = 134,131,135 ppm and 137 ppm assign them to the C(9),C(8), C(7), C(11), and C(10) carbon atoms respectively, due to their interaction with H resonance at δ = 7.4, 7.5, 7.8, 7.80 ppm and 7.3 ppm.

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