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Research Article

GOLD(III)-CHLORO-DPPM-ARYLAZOIMIDAZOLE COMPLEXES : SYNTHESIS, SPECTROSCOPIC AND REDOX STUDY.

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Abstract

The complex $[Au^{III}(dppm)Cl_2(tht)_4](OSO_2CF_3)_4$ with ligand addition produce $[Au^{III}(dppm)Cl_2(RaaiR^{/})_2](OTf)_4$ [RaaiR$^{/}$ = *p*-R-C_6H_4-N=N-C_3H_2-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*), CH_2CH_3 (*2*), CH_2Ph (*3*), dppm is diphenylphosphinomethane, OSO_2CF_3 is triflate anion, tht is tetrahydrothiophen]. IR spectra of the complexes show -C=N- and -N=N- stretching near at 1590 and 1370 cm^{-1} and near at 1100, 755, 695, 545, 505 cm^{-1} for dppm. The ^{1}H NMR spectral measurements suggest methylene, –CH_2–, in $[Au_2(dppm)Cl_2(RaaiCH_2CH_3)_2]^{4+}$, giving a complex AB type multiplet splitting while in $[Au_2(dppm)Cl_2(RaaiCH_2Ph)_2]^{4+}$, AB type quartet splitting.

Keywords: Gold(III), arylazoimidazole, NMR, electrochemistry.

Introduction

Au(III) complexes with peptides as potential medical application as anticancer drugs have been investigated and significant part have been reported in past years. Some of them shown that the in vivo experiments give significant anticancer effect [1-4]. The biochemistry of gold with D-penicillamine [6], gluthadione [7], thiomalic acid [8], 2,3-dimercaptopropanol [9], and albumin has been studied. The reactivity of gold occurs though the thiolate function of these biological molecules and leads to the formation of gold(I) thiolates, also called chrysotherapy agents. These complexes are efficient against rheumatoid arthrisis and even HIV and are commercialized under different trade names such as Myochrysine, Solganol, Krysolgan, and Allochrysine. Other types of gold complexes used in medicinal chemistry are gold(I) mono- or bis-phosphines. They can bind to DNA via the guanine and cytosine bases [3] and act as antitumor agents against L1210 leukemia and M5076 reticulum cell sarcoma [4]. A small number of scattered observations in the early structural chemistry of gold(I) complexes [1-7] has grown into a wealth of reports on related phenomena in the last two decades, which finally provided a clear pattern of the conditions under which direct interactions between closed-shell gold(I) centers can contribute significantly to the stability of molecular and multidimensional structures [9]. In this paper, the reaction of RaaiR$^{/}$ on gold(III) bis-triphenylphosphine derivatives were examined and the products, $[Au(PPh_3)_2(RaaiR^{/})](OTf)_3$ [RaaiR$^{/}$ = *p*-R-C_6H_4-N=N-C_3H_2-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*), CH_2CH_3 (*2*), CH_2Ph (*3*), OSO_2CF_3 is the triflate anion] were isolated. The complexes were well charecterised by IR, ^{1}H NMR, mass spectrometry.

Experimental

Published methods were used to prepare RaaiR´ [9], $[Au_2^{III}(dppm)(Cl)_6]$ [7-9]. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). The purification of solvents were done following the literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. IR spectra were obtained using a JASCO 420 spectrophotometer (4000-200 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, $CFCl_3$ (external ^{19}F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}$ M in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298 K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE).

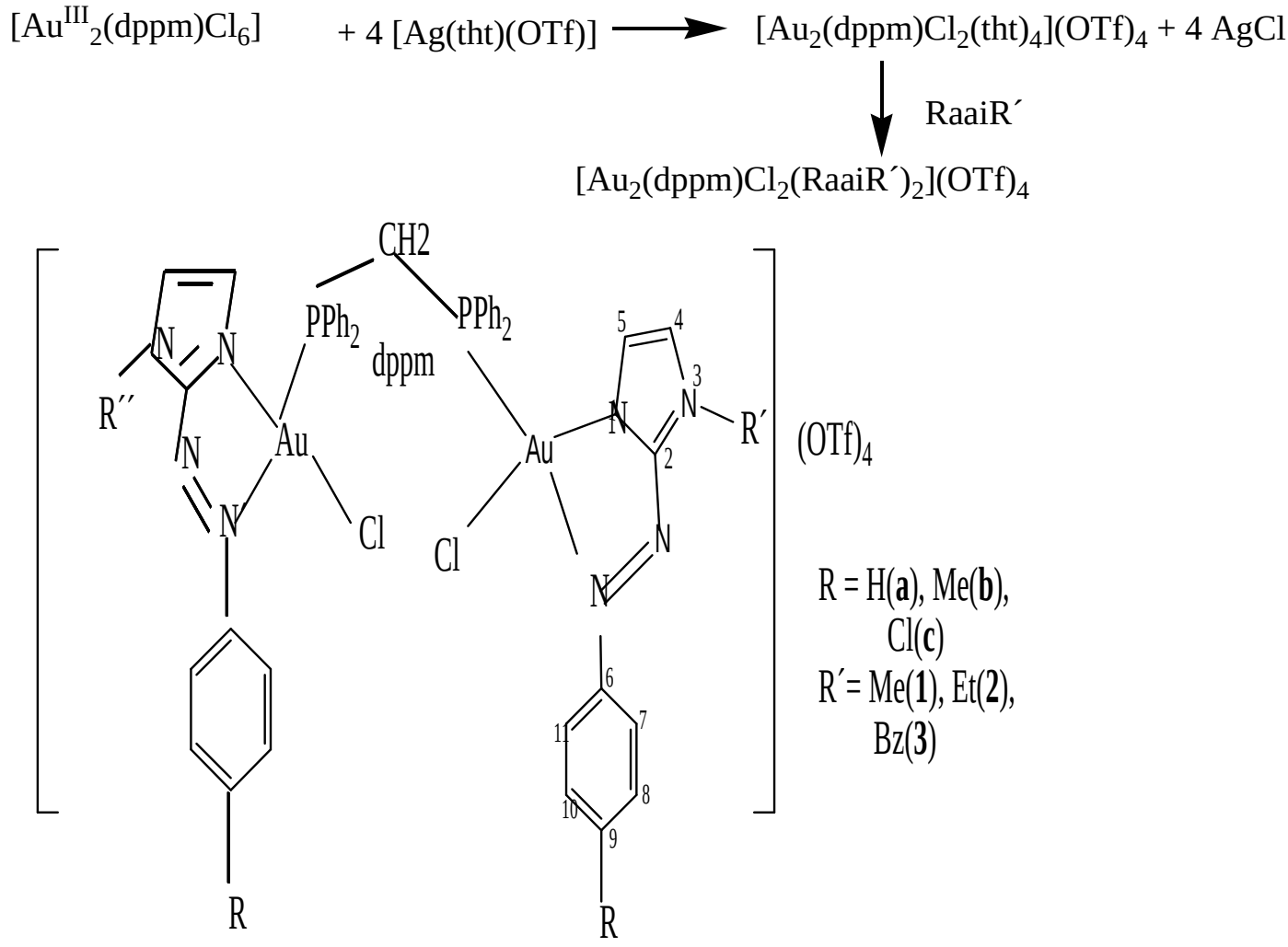
[chloro-(diphenylphosphinomethane){1-ethyl-2-(p-tolylazo)imidazole}aurate(III)]triflate, $[Au^{III}(dppm)Cl(HaaiEt)](OTf)_3$, 2b

To an dichloromethane solution (15 cm^3) of $[Au^{III}(dppm)Cl_6]$ (0.85 g, 0.10 mmol), [Ag(tht)(OTf)] was added (1:4) to produce $[Au^{III}(dppm)Cl_2(tht)_4](OSO_2CF_3)_2$ (1.845 g, 0.40 mmol), and then into this solution, yellow dichloromethane solution of 1-ethyl-2-(p-tolylazo)imidazole was added and the mixture was stirred at 343-353 K for 12 h. Where the other ligands, HeaaiMe (0.036 g, 0.2 mmol, **1a**), MeaaiMe (0.040 g, 0.2 mmol, **1b**), ClaaiMe (0.0440 g, 0.2 mmol, **1c**), HaaiEt (0.040 g, 0.2 mmol, **2a**), MeaaiEt (0.0424 g, 0.2 mmol, **2b**), ClaaiEt (0.0465 g, 0.2 mmol, **2c**), HaaiBz (0.0522 g, 0.2 mmol, **3a**), MeaaiBz (0.0546 g, 0.2 mmol, **3b**), ClaaiBz (0.0587 g, 0.2 mmol, **3c**) were added, respectively. The orange solution that resulted was concentrated (4 cm^3) 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* overnight. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above. Analysis for $[Au^{III}(dppm)Cl_2(HaaiEt)_2](OTf)_4$, found, C, 30.83, H, 2.5, Calcd. For $[C_{46}H_{45}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **2a**, C, 31.0, H, 2.6, IR (nujol, cm^{-1}), ν(N=N) 1370, ν(C=C) 1600 ν(C=N) 1590 ν(dppm) 1100,750,690,550,505; ESIMS, 1788 $[M^+]$, 1188 [M-OTf]; ^1H NMR, ppm, 7.995(d, H(7,11), J = 8Hz), 7.75(d, H(8,10), J=6.5Hz), 7.68(t,J=6Hz,9H), 4.7(dd, 1:2:2:1, J=9Hz, H-Et), 1.99(s, H(Et), 7.57(d, H(4), J=6Hz), 7.58(d, H(5), J=5Hz), 7.31-7.36,7.40-7.56(m, dppm, 30H); ^{19}F $\{^1H\}$NMR,ppm, -78.02(OTf), Analysis for $[Au^{III}(dppm)Cl_2(MeaaiEt)_2](OTf)_4$, found, C, 31.73, H, 2.65, Calcd for $[C_{48}H_{49}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **2b**, C, 31.7, H, 2.7, IR (nujol, cm^{-1}), ν(N=N) 1379, ν(C=C) 1609, ν(C=N) 1590 ν(dppm) 1100,750,690, 550,505; ESIMS, 1816 $[M^+]$, 1216 [M-OTf]; ^{19}F $\{^1H\}$NMR, ppm, -78.02(OTf), ^1H NMR, ppm, 7.99(d, H(7,11), J = 9Hz), 7.75(d, H(8,10), J=6Hz), 1.698(s,9H), 4.72(dd,1:2:2:1, J=9Hz,H-Et), 1.5(9-Me), 1.9(s, H(Et), 7.57(d, H(4), J=6Hz), 7.58(d, H(5), J=5Hz), 7.313-7.362,7.40-7.526(m,dppm,30H); Analysis for $[Au^{III}(dppm)Cl_2(ClaaiEt)_2](OTf)_4$, found, C, 29.83, H, 2.35, calcd. For $[C_{46}H_{43}N8_9P_2Cl_4Au](OSO_2CF_3)_2$, **2c**, C, 29.9, H, 2.4, IR (nujol, cm^{-1}), ν(N=N) 1373, ν(C=C) 1603 ν(C=N) 1595 ν(dppm) 1106,757,698,559,505; ESIMS, 1857$[M^+]$, 1257[M-OTf]; ^1H NMR, ppm, 7.99(d, H(7,11), J = 8Hz), 7.75(d, H(8,10), J=6Hz), 4.6(dd,1:2:2:1, J=9Hz,H-Et), 1.9(s, H(Et), 7.578(d, H(4), J=6Hz), 7.58(d, H(5), J=5Hz), 7.31-7.36,7.40-7.52(m, dppm,30H); $^{19}F\{^1H\}$NMR, ppm, -78.0(OTf), Analysis for $[Au^{III}(dppm)Cl_2(HaaiMe)_2](OTf)_4$, found, C, 30.03, H, 2.3, calcd. For $[C_{44}H_{41}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **1a**, C, 30.0, H, 2.2, IR (nujol, cm^{-1}), ν(N=N) 1379, ν(C=C) 1610 ν(C=N) 1599 ν(dppm) 1100,759,690,559,515; ESIMS, 1760 $[M^+]$, 1160 [M-OTf]; ^1H NMR, ppm, 7.95(d, H(7,11), J = 8Hz), 7.77(d, H(8,10), J=6Hz), 7.6(t,J=6Hz,9H), 1.99(s, H(Me), 7.58(d, H(4), J=6Hz), 7.52(d, H(5), J=5Hz), 7.31-7.32,7.40-7.56(m, dppm,30H); $^{19}F\{^1H\}$NMR, ppm, -78.02(OTf), Analysis for $[Au^{III}(dppm)Cl_2(MeaaiMe)_2](OTf)_4$, found, C, 30.87, H, 2.5, calcd. For $[C_{46}H_{45}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **1b**, C, 30.9, H, 2.6, IR (nujol, cm^{-1}), ν(N=N) 1370, ν(C=C) 1610 ν(C=N) 1596 ν(dppm) 1100,750,690, 550,505; ESIMS, 1788 $[M^+]$, 1188 [M-OTf]; ^1H NMR, ppm, 7.95(d, H(7,11), J = 8Hz), 7.77(d, H(8,10), J=6.5Hz), 1.1(9-Me),1.9(s, H(Me), 7.58(d, H(4), J=6Hz), 7.52(d, H(5), J=5Hz), 7.31-7.32,7.40-7.56(m, dppm,30H); $^{19}F\{^1H\}$NMR, ppm, -78.02(OTf), Analysis for $[Au^{III}(dppm)Cl_2(ClaaiMe)_2](OTf)_4$, found, C, 28.83, H, 2.15, calcd for $[C_{44}H_{39}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **1c**, C, 28.9, H, 2.2, IR (nujol, cm^{-1}), ν(N=N) 1379, ν(C=C) 1600 ν(C=N) 1590 ν(dppm) 1100,750,690,550,505; ESIMS, 1829$[M^+]$, 1229[M-OTf]; ^1H-NMR, ppm, 7.95(d, H(7,11), J = 8Hz), 7.77(d, H(8,10), J=6Hz), 1.89(s, H(Me), 7.58(d, H(4), J=6Hz), 7.58(d, H(5), J=5Hz), 7.31-7.362,7.40-7.52(m, dppm,30H); $^{19}F\{^1H\}$NMR, ppm, -78.02(OTf), Analysis for $[Au^{III}(dppm)Cl_2(HaaiBz)_2](OTf)_4$, found, C, 35.13, H, 2.56, calcd. For $[C_{56}H_{49}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **3a**, C, 35.2, H, 2.6, IR(nujol, cm^{-1}), ν(N=N) 1370, ν(C=C) 1600 ν(C=N) 1590 ν(dppm) 1100,758,697,550,515; ESIMS, 1912 $[M^+]$, 1312 [M-OTf]; ^1H NMR, ppm, 7.99(d, H(7,11), J = 8Hz), 7.75(d, H(8,10), J=6.5Hz), 7.68(t,J=6Hz,9H), 7.1-7.2(m,Bz) and 5.1(q,1:2:2:1, J=9Hz,H-Bz), 7.57(d, H(4), J=6Hz), 7.582(d, H(5), J=5Hz), 7.31-7.362,7.40-7.526(m, dppm,30H);

$^{19}F\{^{1}H\}$NMR, ppm, -78.02(OTf), Analysis for $[Au^{III}(dppm)Cl_2(MeaaiBz)_2](OTf)_4$, found, C, 35.88, H, 2.75, calcd for $[C_{58}H_{53}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **3b**, C, 36.0, H, 2.8, IR(nujol, cm^{-1}), ν(N=N) 1378, ν(C=C) 1609 ν(C=N) 1599 ν(dppm) 1100,750, 690,550,505; ESIMS, 1940 [M^+], 1340 [M-OTf]; ^{1}H NMR, ppm, 7.99(d, H(7,11), J = 8Hz), 7.757(d, H(8,10), J=6Hz), 1.68(9-Me), 7.1-7.2(m,Bz), 5.0(q,1:2:2:1, J=9Hz,H-Bz), 1.19(s, H(Me), 7.578(d, H(4), J=6Hz), 7.52(d, H(5), J=5Hz), 7.31-7.362,7.40-7.526(m, dppm,30H); $^{19}F\{^{1}H\}$NMR, ppm, -78.02(OTf), Analysis for $[Au^{III}(dppm)Cl_2(ClaaiBz)_2](OTf)_4$, found, C, 33.93, H, 2.35, calcd. For $[C_{56}H_{47}N_8P_2Cl_2Au](OSO_2CF_3)_2$, **3c**, C, 34.0, H, 2.4, IR(nujol, cm^{-1}), ν(N=N) 1378, ν(C=C) 1600 ν(C=N) 1599 ν(dppm) 1100,759,690,559,505; ESIMS, 1981[M^+], 1381[M-OTf]; ^{1}H NMR, ppm, 7.99(d, H(7,11), J = 8Hz), 7.75(d, H(8,10), J=6Hz), 5.0(q,1:2:2:1, J=9Hz,Bz),7.2-7.3(M,Bz), 7.578(d, H(4), J=6Hz), 7.582(d, H(5), J=5Hz), 7.31-7.362,7.40-7.526(m, dppm,30H); $^{19}F\{^{1}H\}$NMR, ppm, -78.02(OTf).

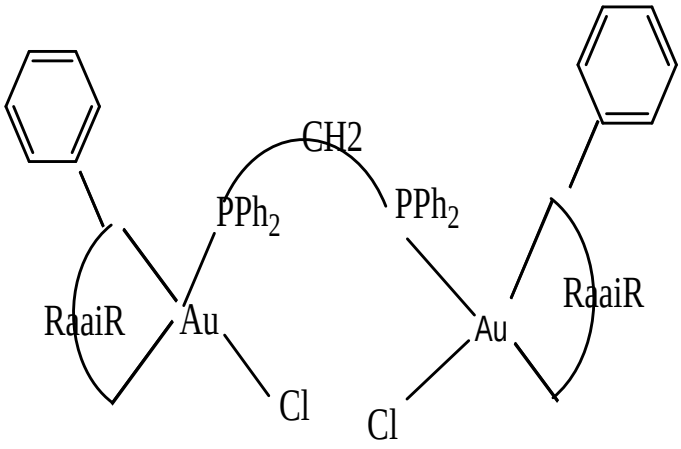
Results and Discussion

The complexes, $[Au^{III}(dppm)Cl_2(RaaiR^{/})_2](OTf)_4$ [RaaiR$^{/}$ = *p*-R-C_6H_4-N=N-C_3H_2-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*), CH_2CH_3 (*2*), CH_2Ph (*3*), OSO_2CF_3 is triflate anion, tht is tetrahydrothiophen], were prepared from $[Au^{III}(dppm)Cl_2(tht)_4](OSO_2CF_3)_4$, under stirring at 343-353 K in good yield (75-80%) (*Scheme 1)*. The composition of the complexes is supported by microanalytical results. The red orange complexes are soluble in common organic solvents viz. acetone, acetonitrile, chloroform, dichloromethane but insoluble in H_2O, methanol, ethanol.

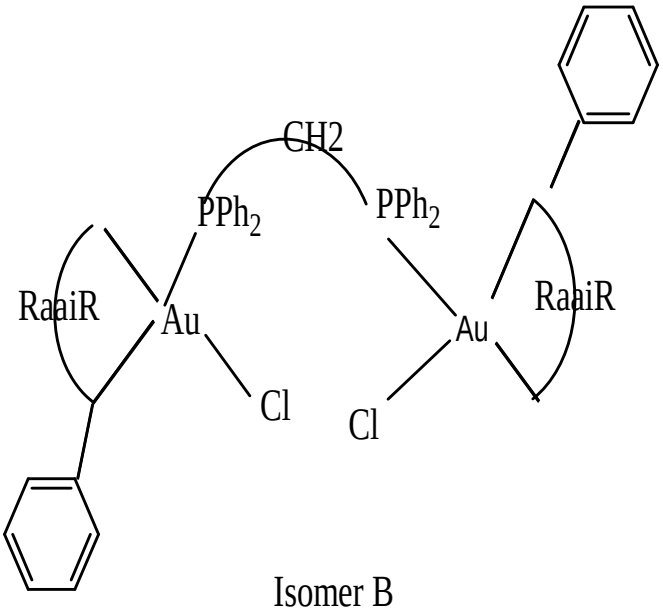


Scheme 1

IR spectra of the complexes, $[Au^{III}(dppm)Cl_2(RaaiR^{/})_2](OTf)_4$ show a 1:1 correspondence to the spectra of the parent chloro analogue (Fig. 1). The spectra show 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 as ν(N=N) and ν(C=N). Other important frequencies are 1110-1120, 1200-1210, 1250-1260, 750-760, 695-700 and 500-510 cm^{-1} along with weak bands at 545-550 cm^{-1} due to dppa. Fluorine NMR, $^{19}F\{^1H\}$, shows a sharp peak at -78 for the presence of triflate anion. The ^1H NMR spectra of the complexes, $[Au^{III}_2(dppm)Cl_2(RaaiR^{/})_2](OTf)_4$ (*1-3*), were assigned (Fig. 1,2) on comparing with parent complex, $[Au_2(dppm)Cl_2]$ and the free ligand ($RaaiR^{/}$). The aryl protons (7-H-11-H) are downfield shifted comparing to those of the parent derivatives. 1-Me appears as a singlet at 2.0 ppm for $[Au_2(dppm)Cl_2(RaaiMe)_2]^{4+}$; the methylene protons, 1-CH_2-(CH_3) show AB type quartet (*ca*. 4.4, 4.6 ppm) and (1-CH_2)CH_3 gives a triplet at 1.5 ppm (7.0-8.0 Hz) for $[Au_2(dppm)Cl_2(RaaiCH_2CH_3)_2]^{4+}$. In the potential range +2.0 to -2.0 V two redox couples are observed prominent and all are at the negative side of the voltammogram. One electron nature of the redox process is supported by the i_{pa}/i_{pc} ratio (i_{pa} = anodic peak current and i_{pc} = cathodic peak current). Two redox couples at negative to SCE are due to reductions of ligand.



Isomer A



Isomer B

TThe azo group in RaaiR´ may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window two reductions were clearly observable.

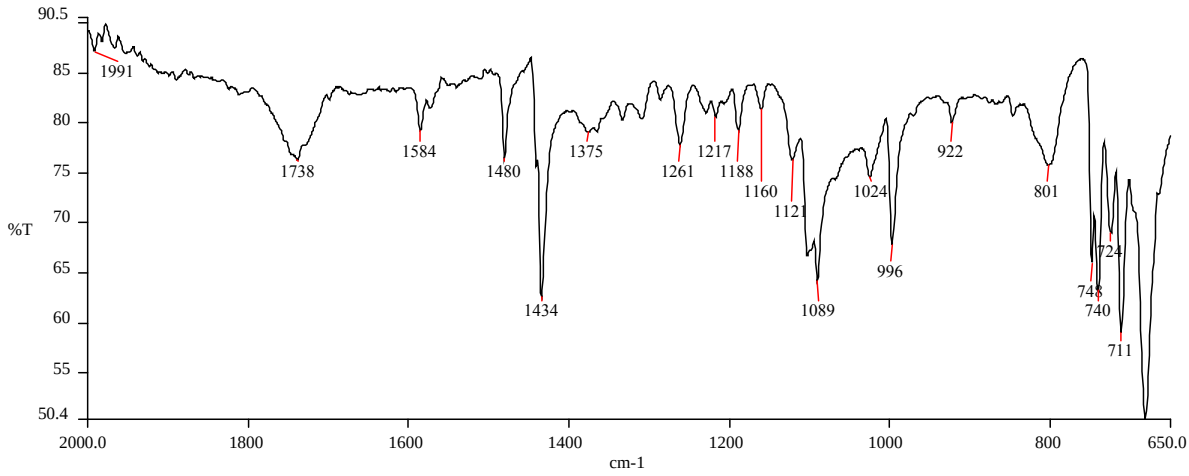
$$[Au_2(dppm)Cl_2(RaaiR´)_2] + e \rightleftharpoons [Au_2(dppm)Cl_2(RaaiR)(RaaiR´^{-})] \quad \text{eq.1}$$

$$[Au_2(dppm)Cl_2(RaaiR)(RaaiR´^{-})] + e \rightleftharpoons [Au_2(dppm)Cl_2(RaaiR´^{2-})] \quad \text{eq2}$$

$$[Au_2(dppm)Cl_2(RaaiR´^{2-})] + e \rightleftharpoons [Au_2(dppm)Cl_2(RaaiR´^{3-})] \quad \text{eq. 3}$$

$$[Au_2(dppm)Cl_2(RaaiR´^{3-})] + e \rightleftharpoons [Au_2(dppm)Cl_2(RaaiR´^{4-})] \quad \text{eq. 4}$$

In conclusion this work describes the isolation of a novel series of Gold(III) arylazoimidazole complexes, $[Au^{III}_2(dppm)Cl_2(RaaiR^{/})_2](OTf)_4$ and their spectral and elemental characterisation. ^1H NMR study suggests quartet splitting of ethyl substitution. Electrochemistry assign ligand reduction part.



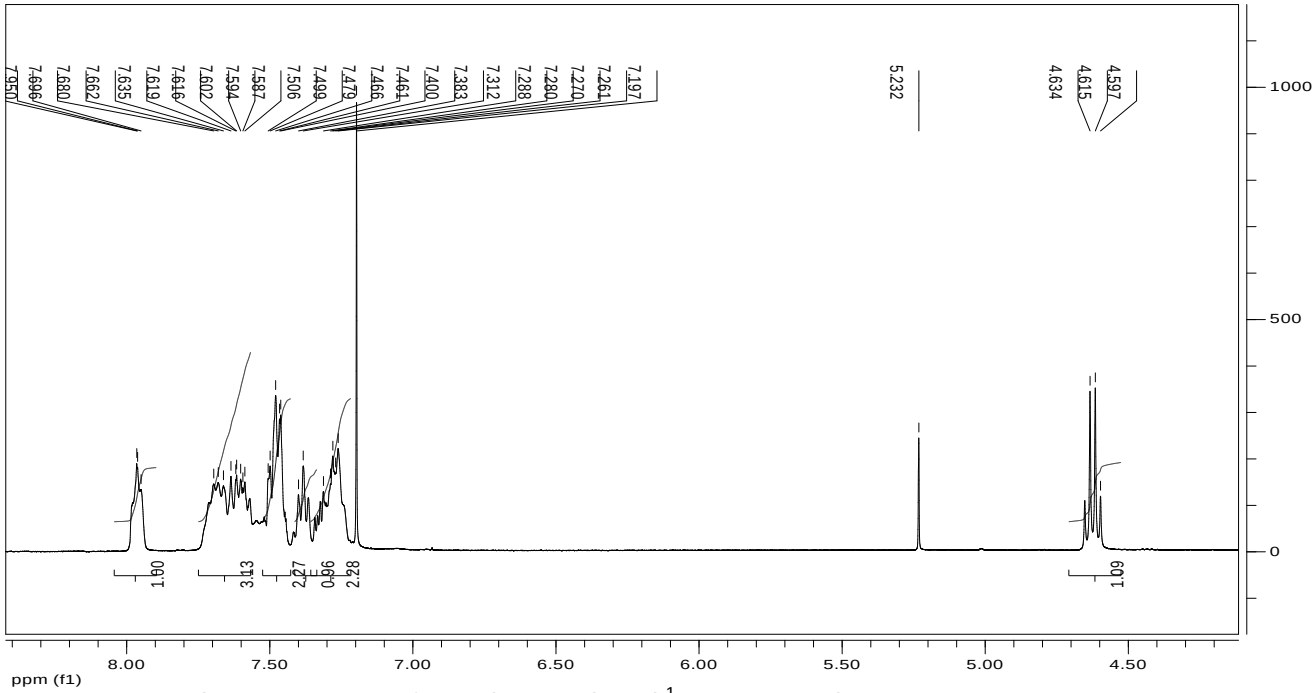


Fig. 1. IR spectra of complex 2a, 2b and ^{1}H NMR complex 2a,

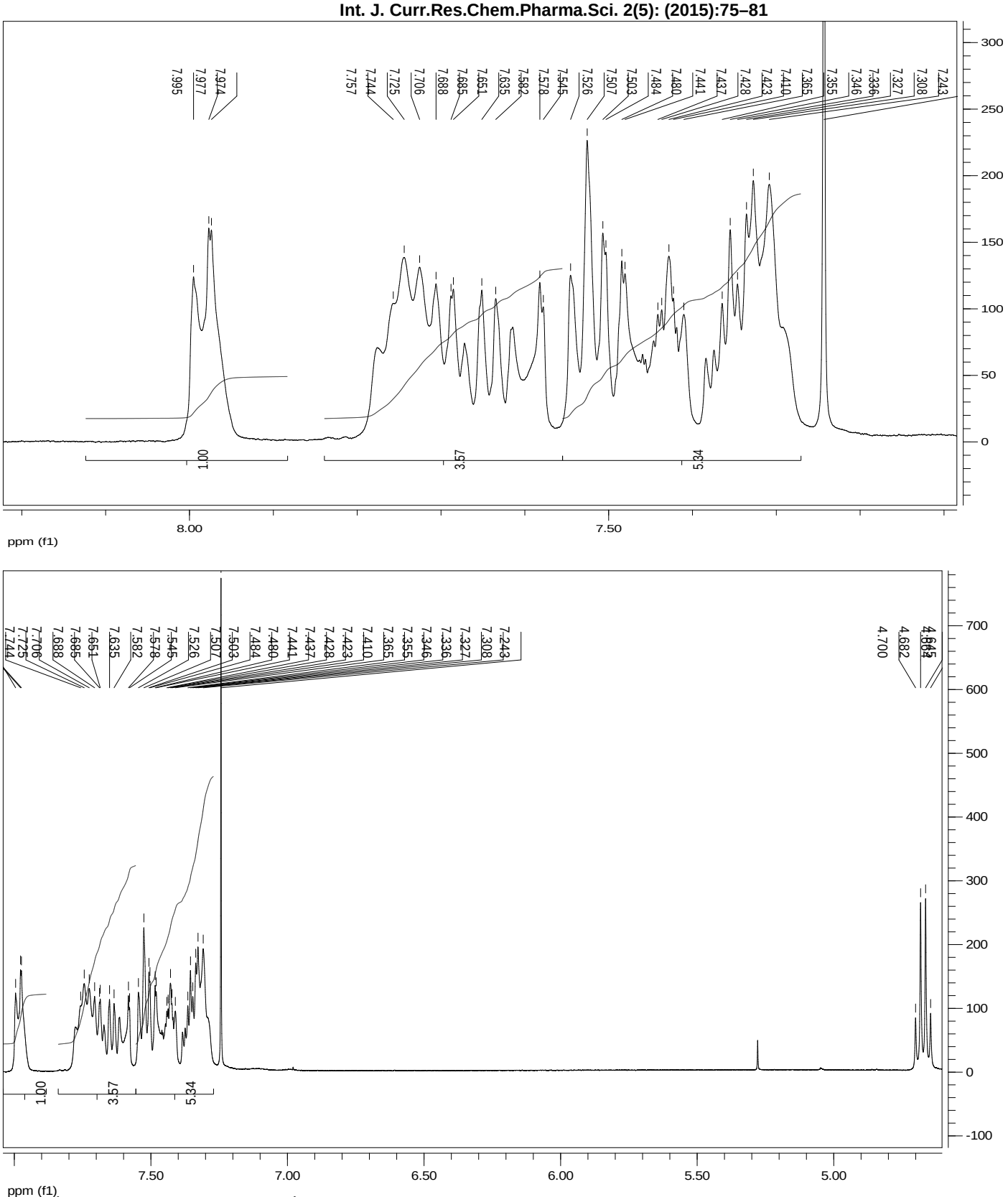


Fig. 2.[1]H NMR of complex 3b and [1]H NMR of complex 2b,

Acknowledgments

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