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Research Article

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Copper(II)-Chloro-triphenylphosphine-arylazoimidazole complexes : Synthesis, Spectroscopic and redox study.

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Abstract

[Ag(tht)(OTf)] assisted reaction produce $[Cu^{II}(PPh_3)Cl(tht)_2](OSO_2CF_3)_2$, reacts with RaaiR´ in dichloromethane medium followed ligand addition leads to $[Cu^{II}(PPh_3)Cl(RaaiR^{/})](OTf)_2$ [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*), PPh_3 is triphenylphosphine, OSO_2CF_3 is the triflate anion, tht is tetrahydrothiophen]. The maximum molecular peak of the corresponding molecule is observed in the ESI mass spectrum. 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, and 505 cm^{-1} due to the presence of triphenylphosphine. The ^1H NMR spectral measurements suggest methylene, –CH_2–, in RaaiEt gives a complex AB type multiplet with coupling constant of av. 6 Hz while in RaaiCH_2Ph it shows AB type quartets with coupling constant of av. 5 Hz. ^{13}C (H)NMR spectrum suggest the molecular skeleton. In the ^1H-^1H COSY spectrum as well as contour peaks in the ^1H-^{13}C HMQC spectrum assign the solution structure. Electrochemistry assign ligand reduction.

Keywords: Copper(II), arylazoimidazole, NMR, electrochemistry

1. Introduction

Running years have witnessed a great deal of interest in the synthesis of the complexes of gold with α-diimine type of ligands because of their photochemical, catalytic properties[2,6,16], energy conversion and ability to serve as building blocks in supramolecular arrays[8-10]. Today in vivo biochemistry of gold remains enigmatic, mainly due to a paucity of adequate models and an inadequate understanding of the reactivity of copper.[4] Moreover, as copper is not a metal naturally used in metabolism, it is believed that its chemistry in vivo differs from other transition metals such as iron and copper, which are carefully transported and stored by enzymatic processes.[5] The biochemistry of copper with D-penicillamine,[6] gluthadione,[7] thiomalic acid,[8] 2,3-

dimercaptopropanol,[9] and albumin[10] has been studied. The reactivity of copper occurs though the thiolate function of these biological molecules and leads to the formation of copper thiolates, also called chrysotherapy agents. These complexes are efficient against rheumatoid arthrisis and even HIV[11] and are commercialized under different trade names such as Myochrysine, Solganol, Krysolgan, and Allochrysine.[12] Other types of copper complexes used in medicinal chemistry are copper (I) mono- or bis-phosphines. They can bind to DNA via the guanine and cytosine bases[13] and act as antitumor agents against L1210 leukemia and M5076 reticulum cell sarcoma.[14] In 1972, Sutton synthesized a copper complex with a thiolate and a phosphine ligand: the 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-pyranosato-*S*-(triethylphosphine) copper (I) compound. It became one of the most promising copper complexes in medicinal chemistry,[15] with a great potency against rheumatoid arthritis and cancer cells such as P388 leukemia and B16.[16] A small number of scattered observations in the early structural chemistry of copper (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 copper (I) centers can contribute significantly to the stability of molecular and multidimensional structures[9]. The underlying "aurophilic" bonding has been analyzed in theoretical studies[1-3]. Syntheses of hetero-*tris*-chelates, $[Ru(bpy)_n(RaaiR^{/})_{3-n}](ClO_4)_2$ [bpy = 2,2′-bipyridine; n = 1, n = 2) containing labile reaction centres are reported from Prof. Sinha´s laboratory [11-21]. Prof. A Chakravorty has unfolded this ligands rhenium chemistry. But the copper chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, I examine the reaction of RaaiR$^{/}$ on copper bis-triphenylphosphine derivatives and the products are isolated, $[Cu(PPh_3)_2(RaaiR^{/})](OTf)_3$ [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*), PPh_3 is triphenylphosphine, OSO_2CF_3 is the triflate anion, tht is tetrahydrothiophen]. The complexes are well charecterised by i.r., ^{1}H n.m.r., ^{13}C nmr, ^{1}H-^{1}H COSY nmr, ^{1}H-^{13}C HMQC and mass spectrometry.

2. Experimental

2.1. Material and instrumentation

Published methods were used to prepare RaaiR$^{/}$[17], $[Cu^{III}(PPh_3)(Cl)]$[17-21]. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). The purification of MeCN used as solvent and other solvents were done following the literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^{1}H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r 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 ~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 298K 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).

2.2. Preparation of the complexes

[chloro-(triphenylphosphine)*{1-ethyl-2-(p-tolylazo)imidazole}aurate(III)]triflate, $[Cu^{II}(PPh_3)Cl(HaaiEt)](OTf)_3$,* ***2b***

To an dichloromethane slight yellow colour solution (15 cm^3) of $[Cu^{II}(PPh_3)ClBr_2]$ (0.665 g, 0.10 mmol) [Ag(tht)(OTf)] was added (1:2) to produce de-bromo product, ie, $[Cu^{II}(PPh_3)Cl(tht)_2](OSO_2CF_3)_2$ (0.945 g, 0.20

mmol) into this, was added yellow dichloromethane 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**), 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 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* over pump overnight. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above.

Analysis for $[Cu^{III}(PPh_3)Cl(HaaiMe)](OTf)_2$, $[C_{28}H_{25}N_4PClCu](OSO_2CF_3)_2$, **1a**, Calc(found): C, 34.3(34.4), H, 2.6(2.69), N, 5. 6(5.7), P, 3.2(3.2); IR ν(N=N) 1370 ν(C=N) 1590 ν(PPh_3) 1100,750,690,550,505; Electrochemistry(dry MeCN), -0.62(90); -0.98(100); Phosphoro n.m.r., $^{31}P\{H\}$, ppm, 36.13; ESIMS, 978.5[M^+], 680.5 [M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^1H, ppm, 8.2(d, H(7,11), J = 8Hz), 8.02(d, H(8,10), J=6.5Hz), 1.99(s, H(CH_3),), 7.26(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 7.1-7.2(m, 15H); Fluoro n.m.r., $^{19}F\{H\}$, ppm, -78.02(OTf), Carbon n.m.r., $^{13}C\{^1H\}$,ppm, 129.1,129.3-130.4(triphenyl phosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42(Me Gr.); Analysis for $[Cu^{III}(PPh_3)Cl(MeaaiMe)](OTf)_2$, $[C_{29}H_{27}N_4PClCu](OSO_2CF_3)_2$, **1b**, Calc(found): C, 35.2(35.1), H, 2.7(2.8), N, 5.6(5.7), P, 3.16(3.15); IR ν(N=N) 1370, ν(C=N) 1590, ν(PPh_3) 1100,750,690,550,505, Electrochemistry(dry MeCN), -0.67(90); -0.91(100); Phosphoro n.m.r., $^{31}P\{H\}$, ppm, 36.14; ESIMS, 992.5[M^+], 694.5[M-2OTf], 721[$Au(PPh_3)_2$], 459[$Au(PPh_3)$]; Proton n.m.r., ^1H, ppm, 8.2 (d, H(7,11), J = 8Hz), 8.09(d, H(8,10),J=6.5Hz), 7.99(dd, H(9), J=7.2Hz), 7.21(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 7.1-7.3(multiplet, PPh_3, 15H), 1.5(Me); Fluoro n.m.r., $^{19}F\{H\}$, ppm , -78.02(OTf), Carbon n.m.r., $^{13}C\{H\}$, ppm, 129.1, 129.3, 130.4 (triphenyl phosphine, 18C), 134.6(C2), 124(C4), 124(C5), 124.3(C7,11), 128.2(C8,10), 134(C6), 42,(Me Gr.); Analysis for $[Cu^{III}(PPh_3)Cl(ClaaiMe)](OTf)_2$, $[C_{28}H_{24}N_4PClCuCl](OSO_2CF_3)_2$, **1c**, Calc(found): C, 33.1(33.18), H, 2.3(2.3), N, 5.5(5.6), P, 3.16(3.17); IR ν(N=N) 1370 ν(C=N) 1595 ν(PPh_3) 1106,759,696,554,505; Electrochemistry(dry MeCN), -0.60(95); -0.98(100); Phosphoro n.m.r., $^{31}P\{H\}$, ppm, 36.83; ESIMS, 1014[M^+], 716[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^1H, ppm, 8.2(d, H(7,11),J = 8Hz), 8.01(d, H(8,10),J=6Hz), 7.26(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 7.5-7.7(multiplet, PPh_3,30H), 1.5(Me); Fluoro n.m.r., $^{19}F\{H\}$, ppm, -78.02(OTf), Carbon n.m.r., $^{13}C\{H\}$, ppm , 129.1,129.3-130.4 (triphenyl phosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129(C8,10), 134(C6), 40(Me Gr.); Analysis for $[Cu^{III}(PPh_3)Cl(HaaiEt)](OTf)_3$, $[C_{29}H_{27}N_4PClCu](OSO_2CF_3)_2$, **2a**, Calc(found): C, 35.2(35.1), H, 2.7(2.8), N, 5.61(5.6), P, 3.16(3.15); IR ν(N=N) 1370, ν(C=N) 1590, ν(PPh_3) 1109,759,699,550,505; Electrochemistry(dry MeCN), -0.69(120); -0.91(90); Phosphoro n.m.r., $^{31}P\{H\}$, ppm, 36.4; ESIMS, 992.5[M^+],694.5[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^1H, ppm, 8.23(d, H(7,11),J = 8Hz), 8.19(d, H(8,10), J=6Hz), 7.99(dd, H(9),J=7Hz), 7.21(d, J=6Hz H(4),), 7.34(d, H(5), J=5Hz), 7.5-7.7(multiplet, 15H PPh_3,), 4.57(quartet, CH_2 of Et, J=5.9Hz), 1.5(t, CH_3 of Et, J=7Hz); Fluoro n.m.r., $^{19}F\{H\}$, ppm, -78.02(OTf). Carbon n.m.r., $^{13}C\{H\}$, ppm, 129.1,129.3,130,130.4(triphenyl phosphine, 18C), 134(C2), 124(C4), 124(C5), 124.3(C7,11), 128.2(C8,10), 134(C6), 42,50(Et Gr.); Analysis for $[Cu^{II}(PPh_3)Cl(ClaaiMe)](OTf)_2$, $[C_{29}H_{26}N_4PClCuCl](OSO_2CF_3)_2$, **2c**, Calc(found): C, 33.9(33.92), H, 2.5(2.5), N, 5.6(5.7), P, 3.1(3.0); IR ν(N=N) 1370, ν(C=N) 1590, ν(PPh_3) 1100,759,690,559,505; Electrochemistry(dry MeCN), -0.60(90); -0.91(80); Phosphoro n.m.r., $^{31}P\{H\}$, ppm, 36.19;

ESIMS, 1027[M^+], 729[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^{1}H, ppm, 8.27(d, H(7,11), J = 8Hz), 8.11(d, H(8,10), J=6.5Hz), 7.26(d, H(4),J=6Hz), 7.34(d, H(5),J=5Hz), 7.5-7.7(multiplet, PPh_3, 15H), 4.5(quartet, CH_2 of Et, J=5.9Hz), 1.5(t, CH_3 of Et, J=6Hz); Fluoro n.m.r., ^{19}F{H}, ppm, -78.02(OTf). Carbon n.m.r., ^{13}C{H}, ppm, 129.1,129.3,130,130.4(triphenyl phosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,50(Et Gr.); Analysis for $[Cu^{III}(PPh_3)Cl(MeaaiEt)_2](OTf)_2$, $[C_{30}H_{29}N_4PClCu](OSO_2CF_3)_2$, **2b**, Calc(found): C, 35.7(35.7), H, 2.9(2.9), N, 5.6(5.7), P, 3.15(3.1); IR ν(N=N) 1374, ν(C=N) 1599, ν(PPh_3) 1105,756,699,559,505, Electrochemistry(dry MeCN), -0.60(90); -0.90(80); Phosphoro n.m.r., ^{31}P{H}, ppm, 36.54; ESIMS, 1006.5[M^+], 708.5[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^{1}H, ppm, 8.2(d, H(7,11), J = 8Hz), 8.11(d, H(8,10), J=7Hz), 7.99(dd, H(9-H), J=7.8Hz), 7.26(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 7.1-7.3(multiplet, PPh_3, 15H), 4.57(quartet, CH_2 of Et, J=5.9Hz), 1.56(t, CH_3 of Et, J=6Hz); Fluoro n.m.r., ^{19}F{H}, ppm, -78.02(OTf), Carbon n.m.r., ^{13}C{H}, ppm, 129.1,129.3,130,130.4(triphenylphosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,50(Et Gr.); Analysis for $[Cu^{III}(PPh_3)Cl(HaaiBz)](OTf)_2$, $[C_{34}H_{29}N_4PClCu](OSO_2CF_3)_2$, **3a**, Calc(found): C, 38.6(38.7), H, 2.81(2.8), N, 5.36(5.37), P, 2.9(2.9); IR ν(N=N) 1376, ν(C=N) 1590, ν(PPh_3) 1107,759,699,559,505; Electrochemistry(dry MeCN), -0.62(90); -0.90(80); Phosphoro n.m.r., ^{31}P{H}, ppm, 36.93; ESIMS, 1054.5[M^+], 756.5[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^{1}H, ppm, 8.27(d, H(7,11), J = 8Hz), 8.21(d, H(8,10),J=7Hz), 7.26(d, H(4),J=6Hz), 7.34(d, H(5), J=5Hz), 7.1-7.3(multiplet, PPh_3, 15H), 4.57(quartet, CH_2 of Bz, J=5.9), 7.3-7.4(Ph of Bz); Fluoro n.m.r., ^{19}F{H}, ppm, -78.02(OTf), Carbon n.m.r., ^{13}C{H}, ppm , 130.2,130.5,129.1,129.3-130.4 (triphenyl phosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42(Bz Gr.); Analysis for $[Cu^{III}(PPh_3)Cl(MeaaiBz)](OTf)_2$,

$[C_{35}H_{31}N_4PClCu](OSO_2CF_3)_2$, **3b**, Calc(found): C, 39.3(39.3), H, 2.9(2.8), N, 5.26(5.29), P, 2.9(2.8); IR ν(N=N) 1374, ν(C=N) 1595, ν(PPh_3) 1100,755,691,559,501, Electrochemistry(dry MeCN), -0.62(90); -0.92(80); Phosphoro n.m.r., ^{31}P{H}, ppm, 36.83; ESIMS, 1068.5[M^+], 770.5[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^{1}H, ppm, 8.07(d, H(7,11), J = 8Hz), 8.01(d, H(8,10), J=6Hz), H(CH_3), 1.99(s,), 7.26(d, H(4), J=6Hz), 7.34(d, H(5), J=5Hz), 7.1-7.4(multiplet, PPh_3,15H), 4.66(quartet, CH_2 of Bz, J=5.9Hz), 7.4-7.45(Ph of Bz); Fluoro n.m.r., ^{19}F{H}, ppm, -78.02(OTf), Carbon n.m.r., ^{13}C{H}, ppm, 129.1,129.3-130.4(triphenyl phosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6); Analysis for $[Cu^{II}(PPh_3)Cl(ClaaiBz)](OTf)_2$, $[C_{34}H_{28}N_4PClCuCl](OSO_2CF_3)_2$, **3c**, Calc(found): C, 37.5(37.7), H, 2.6(2.6), N, 5.16(5.17), P, 2.82(2.8); IR ν(N=N) 1377, ν(C=N) 1590, ν(PPh_3) 1100,750,690,559,505, Electrochemistry(dry MeCN), -0.66(90); -0.96(120); Phosphoro n.m.r., ^{31}P{H}, ppm, 36.84; ESIMS, 1089[M^+], 791[M-2OTf], 721[$Cu(PPh_3)_2$], 459[$Cu(PPh_3)$]; Proton n.m.r., ^{1}H, ppm, 8.2(d, H(7,11), J = 8Hz), 8.1(d, H(8,10), J=6.5Hz), 7.26(d, H(4),J=6Hz), 7.34(d, H(5), J=5Hz), 7.1-7.3(multiplet, PPh_3, 30H), 5.05(quartet, CH_2 of Bz, J=5.9Hz), 7.3-7.4(Ph of Bz); Fluoro n.m.r., ^{19}F{H}, ppm, -78.02(OTf), Carbon n.m.r., ^{13}C{H}, ppm ,129.1,129.3-130.4(triphenyl phosphine, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6).

3. Results and Discussion

3.1. Synthesis and formulation

The complexes, $[Cu^{II}(PPh_3)Cl(RaaiR^/)](OTf)_2$ [$RaaiR^/$ = *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*), PPh_3 is triphenylphosphine, OSO_2CF_3 is the triflate anion, tht is tetrahydrothiophen], were prepared by removing

tht from $[Cu^{II}(PPh_3)Cl(tht)_2]$ $(OSO_2CF_3)_2$, with RaaiR´ under stirring at 343-353 K in dichloromethane solution in good yield (75-80%). 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. In MeCN, the complexes, (*1-3)* behave as 1:2 electrolytes (Λ_M = 60-90 $\Omega^{-1}cm^{-1}mol^{-1}$).

3.2. Spectral studies

I.r. spectra of the complexes, $[Cu^{II}(PPh_3)Cl(RaaiR^{/})](OTf)_2$ show a 1:1 correspondence to the spectra of the bromo analogue, except the appearance of intense stretching at 1365-1370 and 1570-1580 cm^{-1} with concomitant loss of ν(Cu-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 (Fig 1). Other important frequencies are ν(PPh_3) at 1110-1120, 1200-1210, 1250-1260, 750-760, 695-700 and 500-510 cm^{-1} along with weak bands at 545-550cm^{-1}.

The ESI mass spectrum of a MeCN solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic singly. Population of gas phase ions generated by ESI often closely reflects that in solution (Fig. 4).

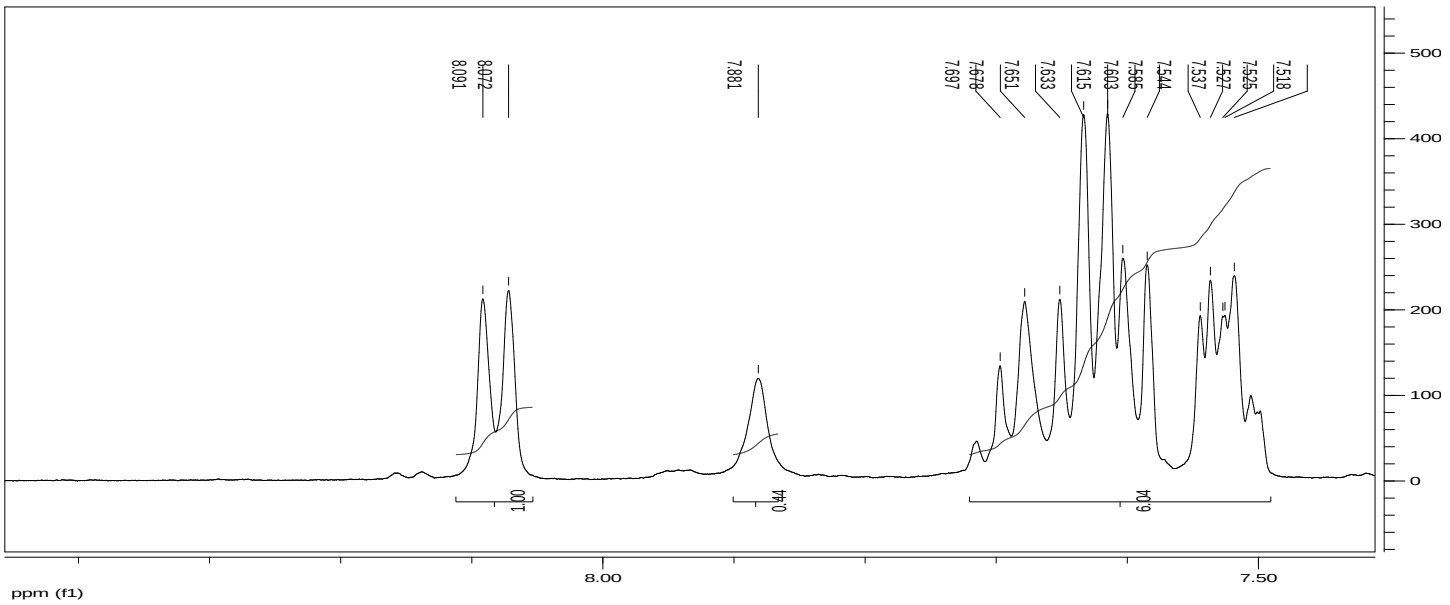
Phosphora n.m.r., ^{31}P {^{1}H}nmr, gives a concrete idea on the nature of complexes and is very much informative of the present series of complexes. Due to the presence of azo-imine function, which is pi acidic in nature, stabilises the gold (III) oxidation state giving the value of 36.3 where the parent bromo complex shows the peak at 41.78 and 31.98 due to *cis trans* isomer mixture, at 45.01 of $[Cu^{II}(PPh_3)_2](OTf)$, at 31.31 of $[Cu^{II}(PPh_3)ClBr_2]$. Changing the substitution at R, R´ on the ligand there is a slight chemical shift value changes of these complexes (Fig. 2,3).

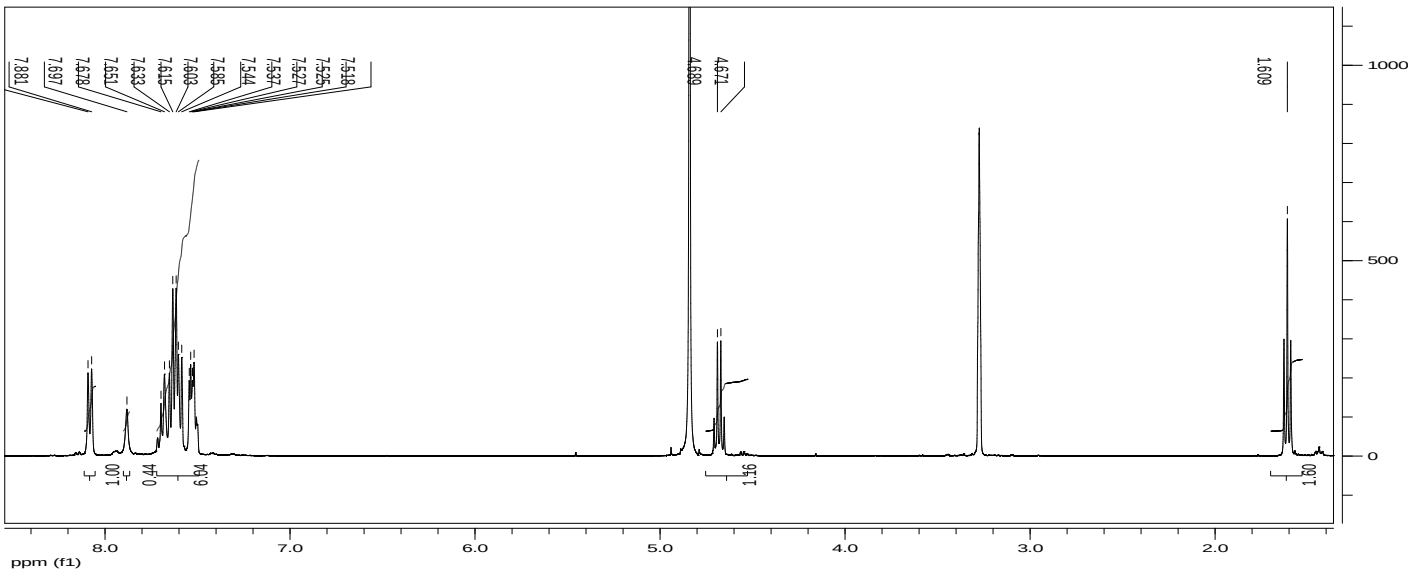
Fluorine n.m.r., ^{19}F{H}, of the present series of complexes show a sharp peak at -78 for the presence of triflate ion.

The ^{1}H n.m.r. spectra of $[Cu^{II}(PPh_3)Cl(RaaiR^{/})](OTf)_2$ (*1-3*) complexes were unambiguously assigned (Figure 1,2 and 4) on comparing with $[Cu(PPh_3)ClBr_2]$ and the free ligand $(RaaiR^{/})$[17,21]. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The aryl protons (7-H-11-H) of (*7-9)* are downfield shifted by 0.1-0.7 ppm as compared to those of the parent derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9)-position. Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The aryl protons 7-($7^{/}$-) and 11-($11^{/}$-)H resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution phase. The 1-$R^{/}$ [$R^{/}$ = Me, CH_2CH_3, CH_2(Ph)] exhibit usual spin-spin interaction. 1-Me appears as a singlet at 2.0 ppm for $[Cu(PPh_3)Cl(RaaiMe)]^{2+}$; 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 $[Cu(PPh_3)Cl(RaaiCH_2CH_3)]^{2+}$. 1-CH_2(Ph) protons appear at AB type quartets (ca. 5.5, 5.7 ppm) with geminal coupling constant avg. 8.8 Hz in $[Cu(PPh_3)Cl(RaaiCH_2Ph)]^{2+}$.

The ^{13}C (H)NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms are done on nine complexes and the data are given on experimental section (Fig 3,2). 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 the methyl, ethyl, benzyl substituted imidazole rings and the pi electron delocalization on the =N-CC=N- and =N-CC=CC-. Similarly the carbon atom adjacent to the PPh_3 molecule in the complex resonance at a lower field resulting of the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The

methyl carbon atom of the imidazole ring resonate at 30 ppm, resonably compare to the other carbon atoms resonance. In the COSY spectrum, absence





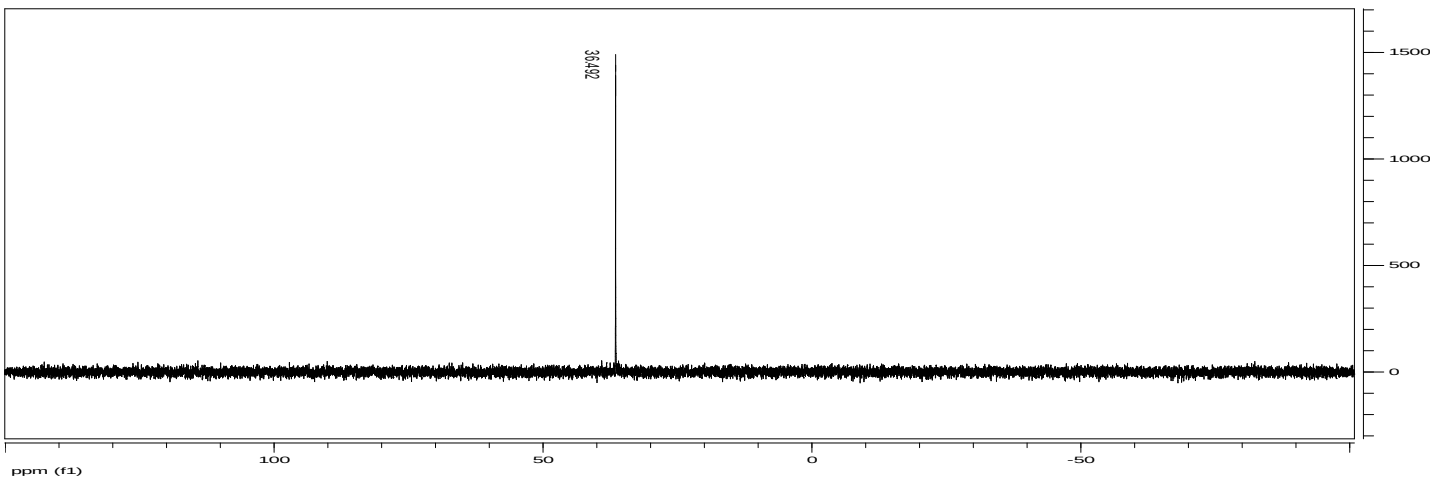
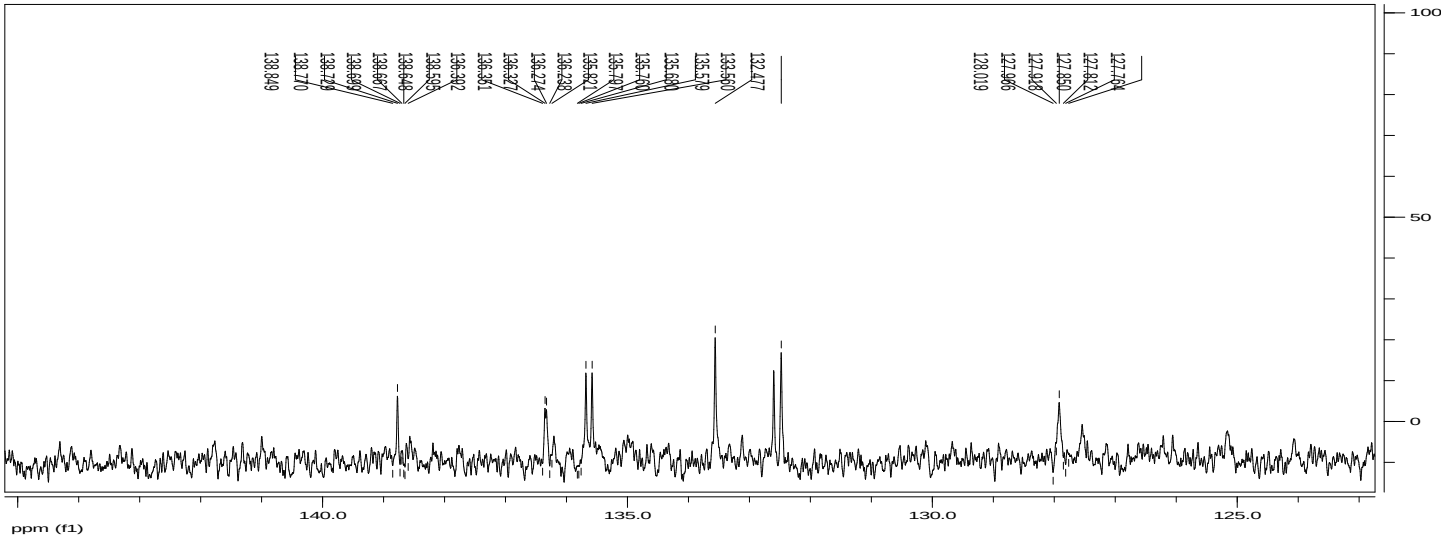
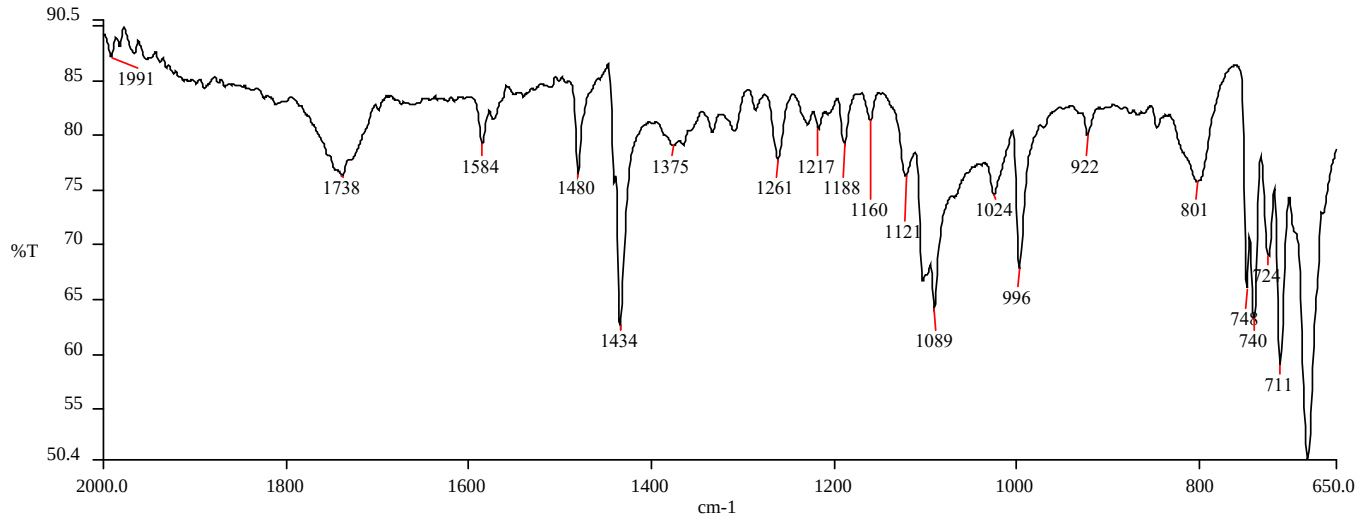


Fig. 1. From above, H NMR of complex 2a 2b and P (H)NMR of complex 2a,





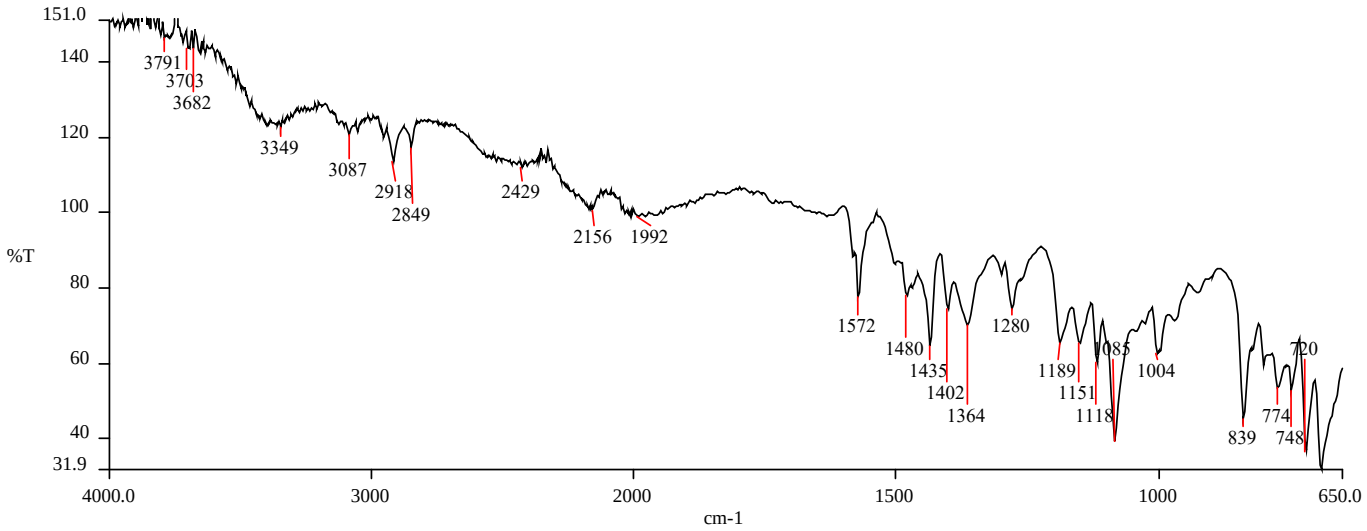


Fig. 2. above, C (H)NMR of complex 2a and below, IR spectra of complex 2a and 2b

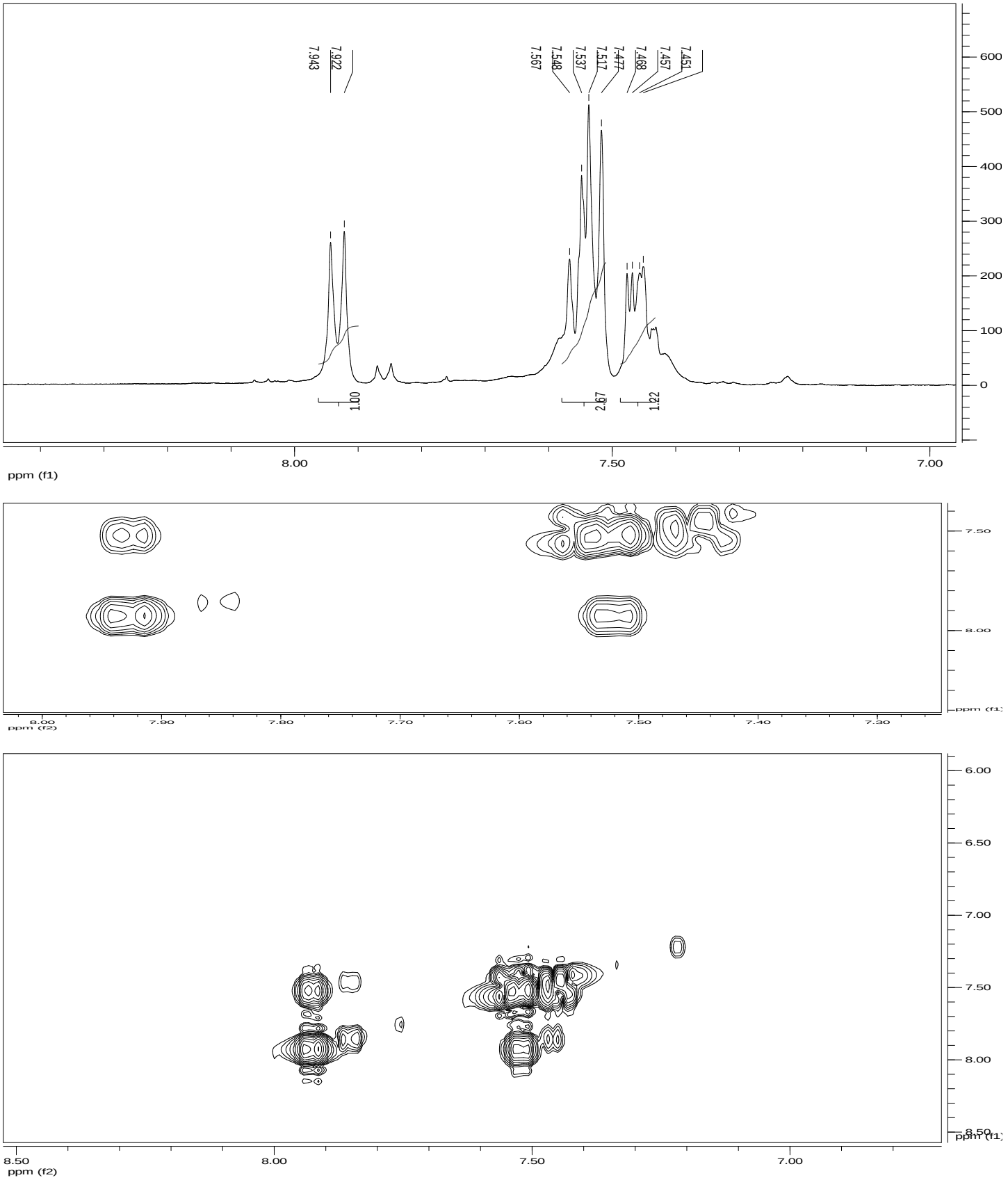


Fig. 3. H NMR of complex 2c and H H COSY NMR of complex 2c, extended portion

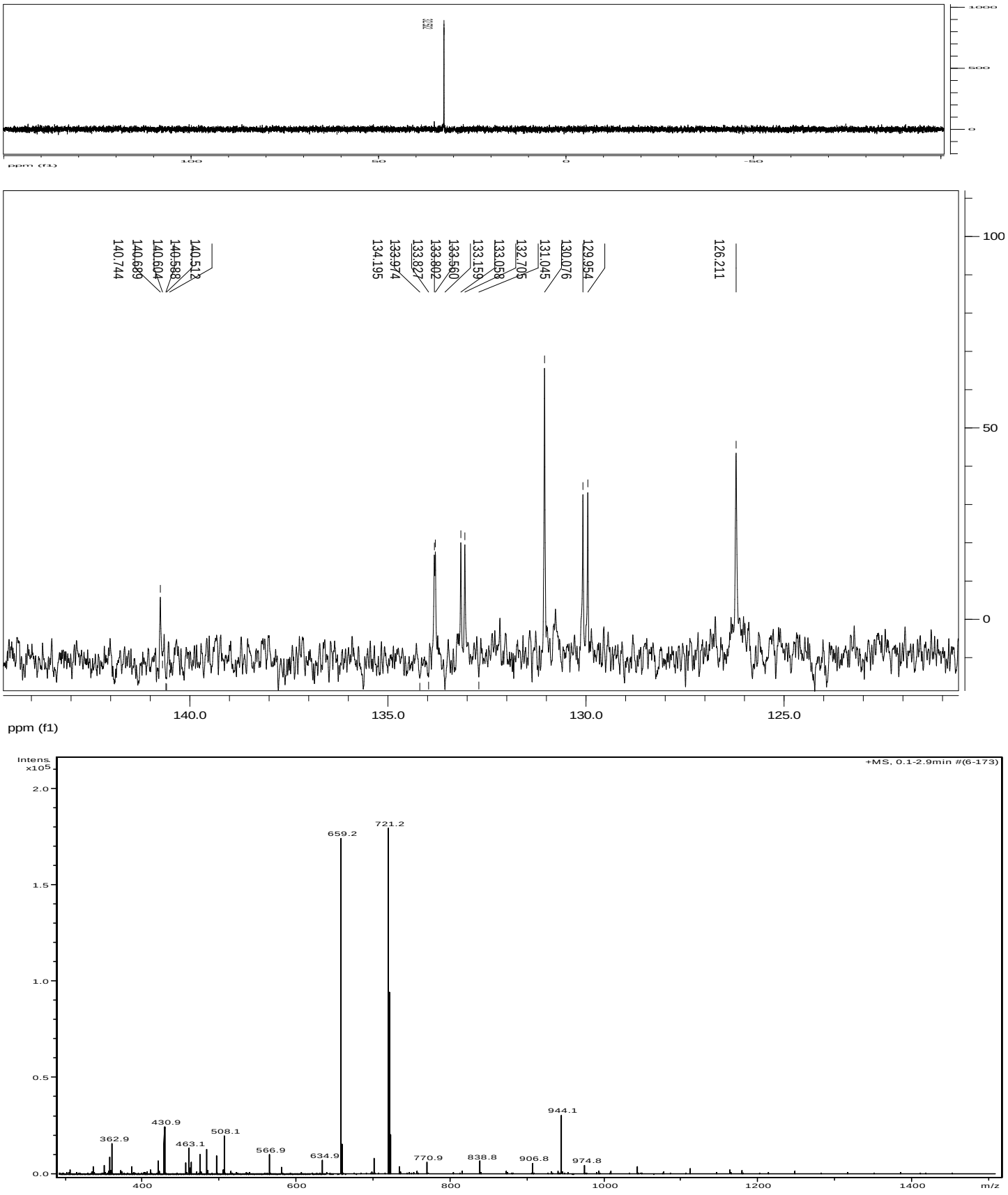


Fig. 4., P (H)NMR of complex 2c, C (H)NMR of complex 2c, ESI mass spectra of 2b

of any off-diagonal peaks extending from δ = 14.1 ppm and 9.5 ppm confirm their assignment of no proton on N(1) and N(3) respectively. However, 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 = 7.1 ppm and 7.2 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The comperatively weaker coupling interactions of C(8)H and C(10)H with the far apart positioned C(4)H and C(5)H protons of the imidazole moity are shown by the poorly resolved cross peaks at δ = 7.3 ppm and 7.31 ppm. The ^{1}H-^{13}C heteronuclear multiple-quantum coherence (HMQC) spectrum provides information regarding the interaction between the protons and the carbon atoms to which they are directly attached. Here, the absence of any contours at higher frequency region assign them C2, C6, C-ipso, carbon atoms respectively. This is because, they belong to the non-protonated carbon atoms on the imidazole, phenyl and aryl rings. So they are unable to show any direct ^{1}H-^{13}C heteronuclear multiple-quantum coherence. 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.

The electrochemical properties of the complexes were examined cyclic voltammetrically at a glassy carbon working electrode in MeCN and the potentials are referred to SCE. The voltammogram show the ligand reductions at the negative to SCE. In the potential range +2.0 to -2.0 V at the scan rate 50 mV s^{-1} two redox couples are observed prominent and all are at the negative side of the voltammogram. First one is quasireversible as is evident from peak-to-peak separation value, ΔE_p>110 mV. The metal oxidation part is very negligible, ie, show a very weak irreversible peak near at 0.5 V mostly in all the cases. 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) which varies -0.60 to –0.79 and -0.90 to -1.05. Two redox couples at negative to SCE are due to reductions of ligand. The 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 as shown below.

4. Conclusion

This work describes the isolation of a novel series of copper (II) azo-imine complexes, $[Cu^{II}(PPh_3)Cl(RaaiR^{/})](OTf)_2$ and their spectral and elemental characterisation. ^{1}H NMR study suggests quartet splitting of ethyl substitution. ^{31}P {^{1}H}NMR is very much informative and they show the sharp signals at 36.13 ppm which is lower than the parent complex, shows the peak at 41.78 and 31.98 due to *cis trans* isomer mixture, at 45.01 of $[Cu(PPh_3)_2](OTf)$, at 31.31 of $[Cu^{II}(PPh_3)ClBr_2]$. ^{13}C (^{1}H)NMR study suggests molecular skeleton. ^{1}H-^{1}H COSY spectrum as well as contour peaks in the ^{1}H-^{13}C HMQC spectrum assign them to the carbon hydrogen atoms interaction. Electrochemistry assign ligand reduction part rather than metal oxidation.

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