Preparations

Ru(pzt)Cl_3, 3. To 125 mL of absolute ethanol in a 200 mL round-bottom flask was added $RuCl_3.3H_3O$ (0.033 g, 0.124 mmol) and ligand pzt (0.070 g, 0.124 mmol). The mixture was heated at reflux for about 3 h while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder which had appeared was filtered from the red-brown solution. The product was washed with 3 × 30 mL portions of diethyl ether and air-dried. Yield 0.0724 g , 75 %.

[Ru(pzt)$_2$](PF_6)$_2$, 4. Ligand pzt (0.083 g, 0.147 mmol) and Ru(pzt)Cl_3 complex (0.072 g, 0.074 mmol) in dry MeOH (50 mL) in presence of *N*-methylmorpholine (12 drops) were heated at reflux for 4h under Ar. The deep red solution was cooled to room temperature before it was filtered to remove any unreacted materials. The solution was taken to dryness under vacuum and the residue was purified by column chromatography (SiO_2 eluting with CH_3CN-saturated KNO_3 solution-H_2O, 10 :2 :1). An excess of NH_4PF_6 was added to the major red-brown fraction and the solution was reduced in volume under vacuum. The precipitate was collected by filtration over Celite, before it was dissolved in CH_3CN, and evaporated to dryness *in vacuo* to afford [Ru(pzt)$_2$](PF_6)$_2$ as a red-brown powder. Yield 0.095g, 79 %. ^{1}H NMR (500 MHz; solvent acetone-d_6, see Table 3). ^{13}C NMR (75 MHz; solvent acetone-d_6) δ 158.8, 156.0, 152.8 (C_6, $C_{6''}$), 148.3, 141.0 (C_{03}, $C_{03'}$, $C_{03''}$), 140.5, 138.5 (C_4, $C_{4''}$), 136.4, 131.2 (C_{05}, $C_{05'}$, $C_{05''}$), 128.9 ($C_{3'''}$, $C_{5'''}$) , 128.0 ($C_{2'''}$, $C_{2'''}$, C_5, $C_{5''}$), 125.0 (C_3, $C_{3''}$), 121.7 ($C_{3'}$, $C_{5'}$). 106.4 (C_{05}, $C_{05'}$, $C_{05''}$), 73.4 (C_{01}), 73.06 (C_7). IR (KBr, cm^{-1}): 108.8, 106.4(C_{04}, $C_{04'}$, $C_{04''}$), 73.4 (C_{01}), 73.0 (C_7). IR (KBr, cm^{-1}): 2960 w, 2920 w, 2850 w,1609 msh, 1408 m, 1204 w, 849 ssh, 787 msh, 756 msh, 559 ssh. ES-MS:

m/z 1377.6 ($[M\text{-}PF_6]^+$), 616.3 ($[M\text{-}2PF_6]^{2+}$). UV-vis (CH_3CN): λ_{max} (ε) = 284.9 (68100), 310.0 (62700), 490.1 (22000) nm (L mol^{-1} cm^{-1}).

[(ttp)Ru(pzt)]$(PF_6)_2$, 5. $Ru(ttp)Cl_3$ (0.265 g, 0.50 mmol) was added to pzt (0.283 g, 0.50 mmol) in MeOH (20 mL). 10 drops of *N*-methylmorpholine was added. The solution was heated to reflux with stirring for 1 hr. The resulting deep-red solution was filtered through Celite to remove any unreacted $[Ru(ttp)Cl_3]$ and excess methanolic solution of ammonium hexafluorophosphate was added to the filtrate to precipitate the ligand complexes. Further purification was achieved by column chromatography over silica eluting with CH_3CN-saturated KNO_3 solution-H_2O (17: 0.5: 1). The major orange-red band was collected. The complex was isolated as its PF_6^- salt as a red powder. Yield 0.6 g, 94%. ^1H NMR (500 MHz; solvent acetone-d_6, see Table 3). ^{13}C NMR (75 MHz; solvent acetone-d_6) δ 158.82, 158.74, 156.03, 155.93, 152.82 (C_6, $C_{6''}$), 148.56, 148.19, 141.03 (C_{03}, $C_{03'}$, $C_{03''}$), 140.43, 138.44 (C_4, $C_{4''}$), 136.37, 133.95, 131.16 (C_{05}, $C_{05'}$, $C_{05''}$), 130.43 ($C_{3'''}$(ttp), $C_{5'''}$(ttp)), 128.92 ($C_{3'''}$(pzt), $C_{5'''}$(pzt)) , 128.00 ($C_{2'''}$(pzt), $C_{6'''}$(pzt), C_5(pzt), $C_{5''}$(pzt)), 127.96 ($C_{2'''}$(ttp), $C_{6'''}$(ttp), C_5(ttp), $C_{5''}$(ttp)), 125.00 (C_3, $C_{3''}$), 121.68 ($C_{3'}$(pzt), $C_{5'}$(pzt)), 121.34 ($C_{3'}$(ttp), $C_{5'}$(ttp)), 106.37 (C_{05}, $C_{05'}$, $C_{05''}$), 73.37 (C_{01}), 73.06 (C_7), 20.69 (CH_3(ttp)). IR (KBr, cm^{-1}): 3080 w, 2950 w, 2852 w, 1605 ssh, 1520 m, 1408 msh, 1327 m, 1246 w, 1196 w, 1096 m, 1030 wsh, 949 w, 840 ssh, 787 ssh, 752 msh, 656 wsh, 617 w, 559 ssh, 509 w. ES-MS: *m/z* 1135.5 ($[M\text{-}PF_6]^+$), 495.2 ($[M\text{-}2PF_6]^{2+}$). UV-vis (CH_3CN): λ_{max} (ε) = 284.9 (60900), 310.0 (60400), 490.1 (21300) nm (L mol^{-1} cm^{-1}).

[Cd(pzt)$(NO_3)_2$], 9. To the ligand pzt (0.011 g, 0.02 mmol) in CH_2Cl_2 (5 mL) was added $Cd(NO_3)_2.4H_2O$ (0.006 g, 0.02 mmol) in CH_3CN (5 mL) dropwise under Ar atmosphere. The reaction mixture was stirred at r.t overnight. The clear solution was

filtered. Colourless crystals were obtained upon slow evaporation of the solution at r.t. The crystals were separated by filtration, washed with diethyl ether, then dried under vacuum. Yield 0.009 g, 56%. ^{1}H NMR (500 MHz; solvent dmso-d_6, see Table 3). ^{13}C NMR (75 MHz; solvent dmso-d_6) δ 153.25, 149.76, 149.53, 148.66, 141.22, 141.10, 140.32, 135.29, 131.30, 128.42, 128.27, 127.46, 124.04, 121.06, 106.79, 89.51, 72.82, 72.39. IR (KBr, cm^{-1}): 3113 m, 3078 m, 2947 w, 2893 w, 1701 w, 1601 m, 1574 m, 1551 m, 1516 m, 1481 ssh, 1447 ssh, 1385 ssh, 1296 ssh, 1265 ssh, 1204 m, 1165 m, 111m, 1015 msh, 949 m, 918 m, 895 w, 818 m, 791 ssh, 752 m, 660 w, 640 w, 617 w, 513 w, 451 w. ES-MS: *m/z* (intensity (%), fragment), 1305.3 (1, $[Cd(pzt)_2\text{-}NO_3]^+$), 622.3 (100, $[Cd(pzt)_2\text{-}2NO_3]^{2+}$). Anal. Calc. for $C_{33}H_{27}CdN_{11}O_7$ (802.05): C 49.42, H 3.39, N 19.21%; found: C 49.43, H 3.40, N 18.83%.

$\{\{[Fe(pzt)_2](NO_3)_2\}(AgNO_3)_2\}_\infty$, 10. To complex **6** (0.001 g, 0.0007 mmol) in acetone (1 mL) was added a solution of $AgNO_3$ (0.0003 g, 0.0014 mmol) in acetonitrile (1 mL), dropwise. The mixture was allowed to slowly evaporate in the air at r.t. The microcrystalline solid which formed the reaction mixture was collected, washed with diethyl ether, and air-dried. ^{1}H NMR (500 MHz; solvent acetone-d_6, see Table 3). ES-MS: *m/z* 763.26 ($\{[Fe(pzt)_2Ag_2)](NO_3)_2\}^{2+}$).

$\{\{[Fe(pzt)_2](BF_4)_2\}(AgBF_4)\}_\infty$, 11. To complex **6** (0.001 g, 0.0007 mmol) in acetone (1 mL) was added $AgBF_4$ (0.0003 g, 0.0014 mmol) in acetone (1 mL) dropwise. The mixture was allowed to slowly evaporate in the air at r.t. The microcrystalline compound which was crystallized from the reaction mixture was collected, washed with small amount of cold acetone, and air-dried. ES-MS: *m/z* 691.4 ($\{[Fe(pzt)_2Ag)](BF_4)\}^{2+}$)

{{[Fe(pzt)$_2$](ClO$_4$)$_2$}(AgClO$_4$)$_2$}$_\infty$, 12. Same method was used as above except $AgClO_4$ (0.0003 g, 0.0014 mmol) in acetone (1 mL) was applied instead. ES-MS: *m/z* 801.23 ({[Fe(pzt)$_2$Ag$_2$)](ClO$_4$)$_2$}$^{2+}$)

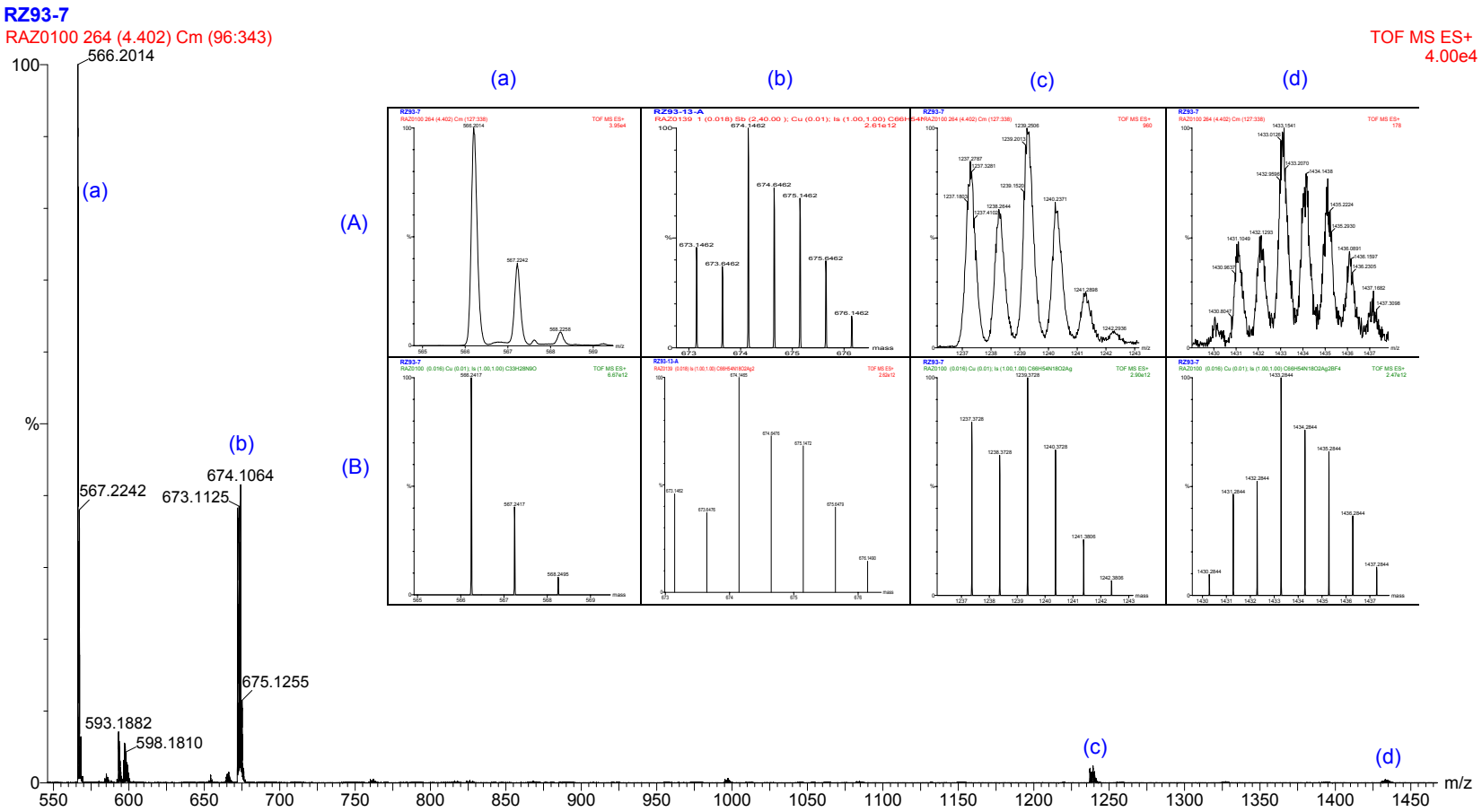

Fig. I. ES-MS of material obtained from the reaction of ligand pzt with $AgBF_4$ in acetone. (A) High resolution scans of the four major signals (a)-(d); (B) Calculated isotope distribution patterns for (a) $[(pztH)]^+$, (b) $[Ag_2(pzt)_2]^{2+}$, (c) $[Ag(pzt)_2]^+$, (d) $[Ag_2(pzt)_2+(BF_4)]^{2+}$.

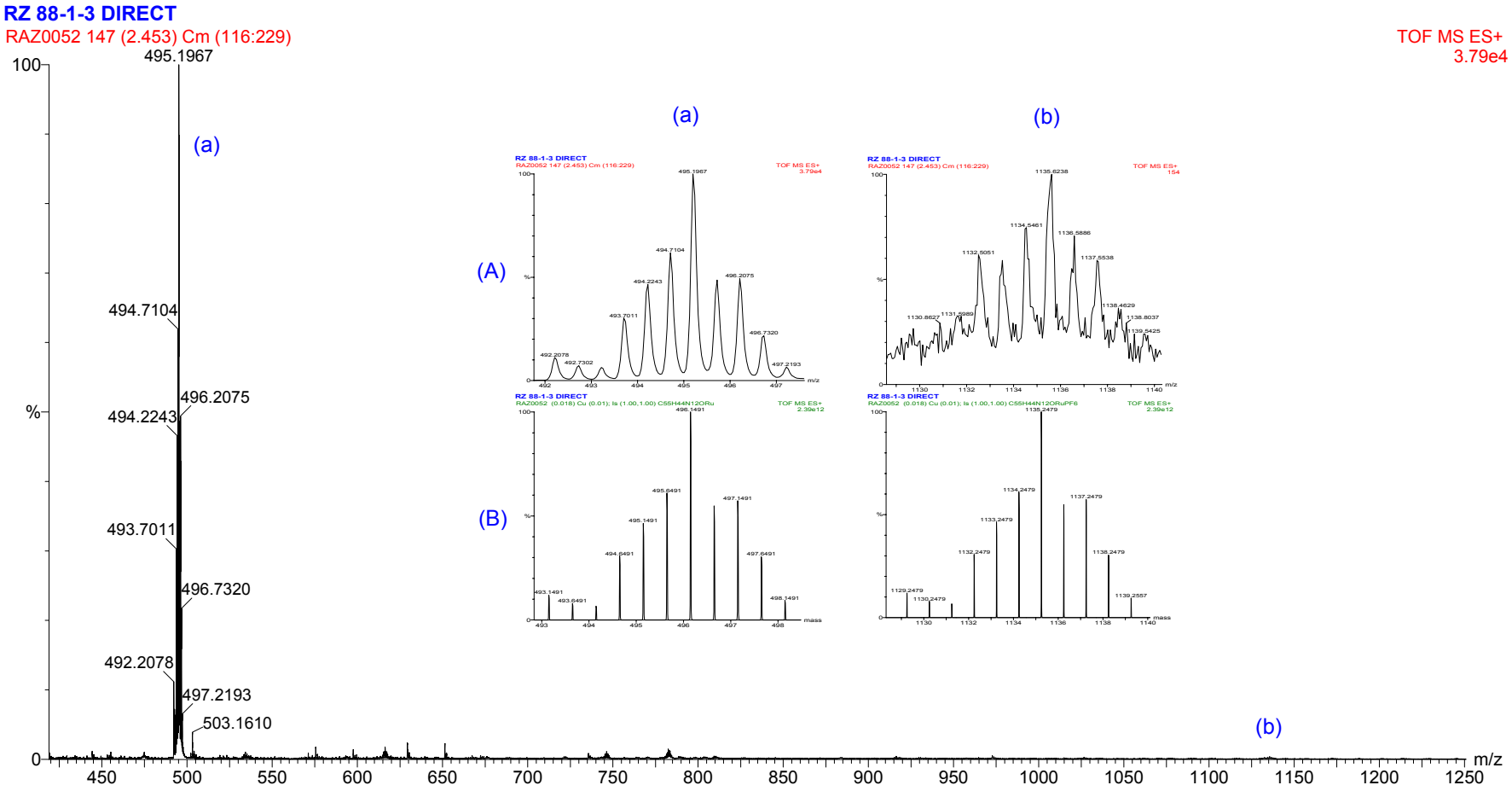

Fig. II. ES-MS of $[Ru(pzt)(ttp)](PF_6)_2$ complex in CH_3CN. (A) High resolution scans of the two signals (a) and (b); (B) Calculated isotope distribution patterns for (a) $[Ru(pzt)(ttp)]^{2+}$ and (b) $[Ru(pzt)(ttp)+(PF_6)]^{+}$.

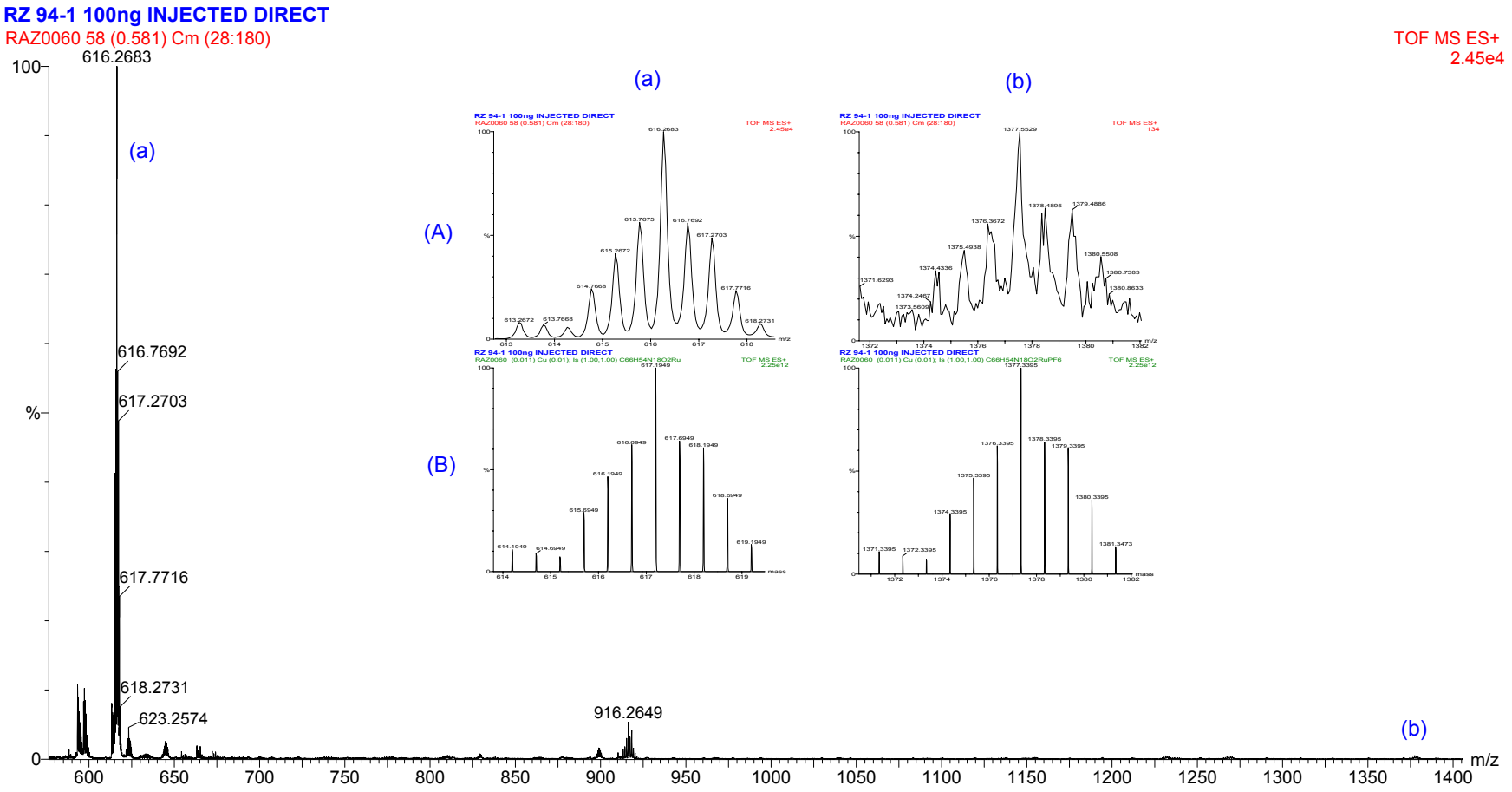

Fig. III. ES-MS of $[Ru(pzt)_2](PF_6)_2$ complex in CH_3CN. (A) High resolution scans of the two major signals (a) and (b); (B) Calculated isotope distribution patterns for (a) $[Ru(pzt)_2]^{2+}$ and (b) $[Ru(pzt)_2+(PF_6)]^{+}$.

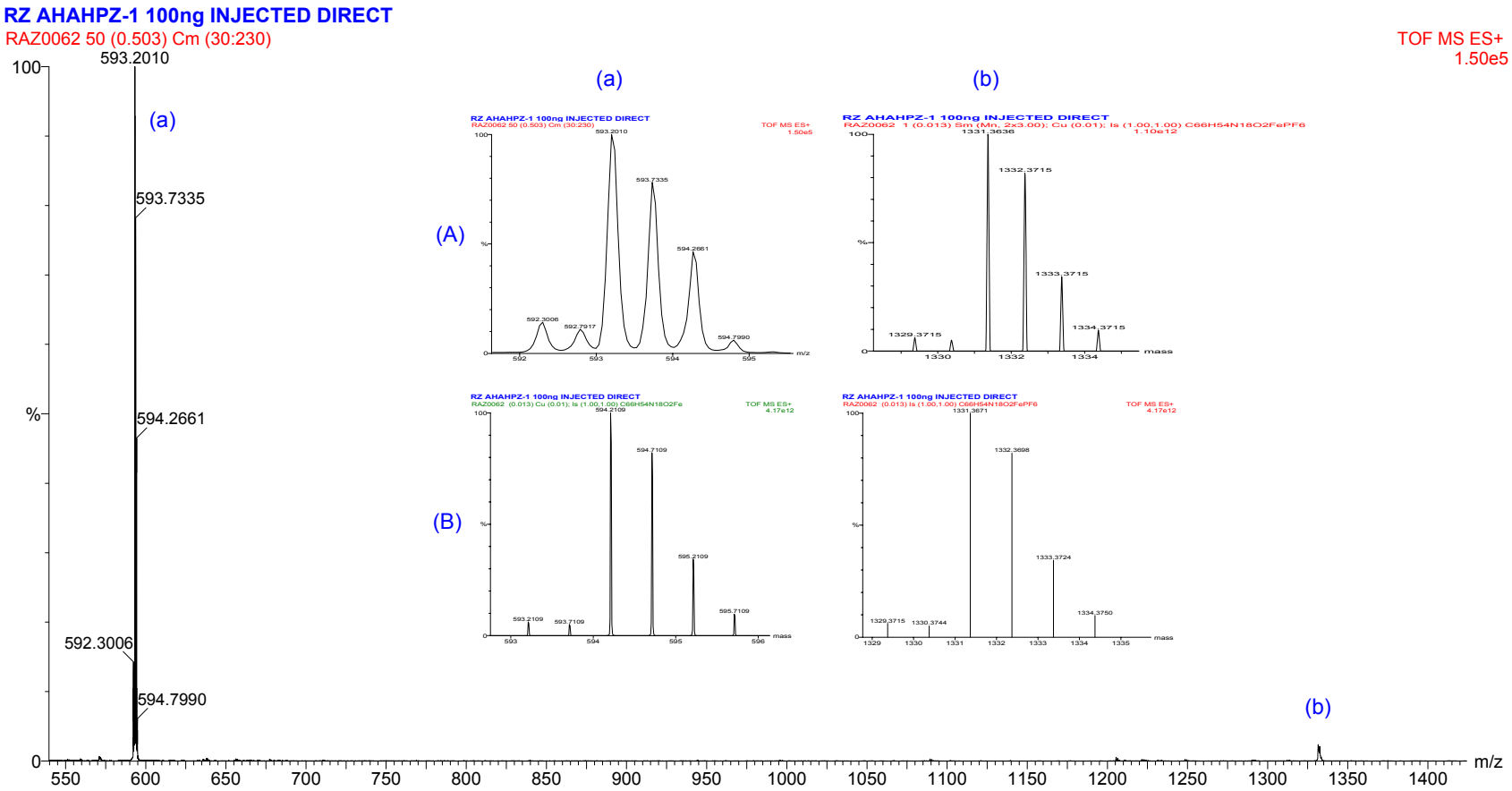

Fig. IV. ES-MS of $[Fe(pzt)_2](PF_6)_2$ complex in CH_3CN. (A) High resolution scans of the two major signals (a) and (b); (B) Calculated isotope distribution patterns for (a) $[Fe(pzt)_2]^{2+}$ and (b) $[Fe(pzt)_2+(PF_6)]^{+}$.

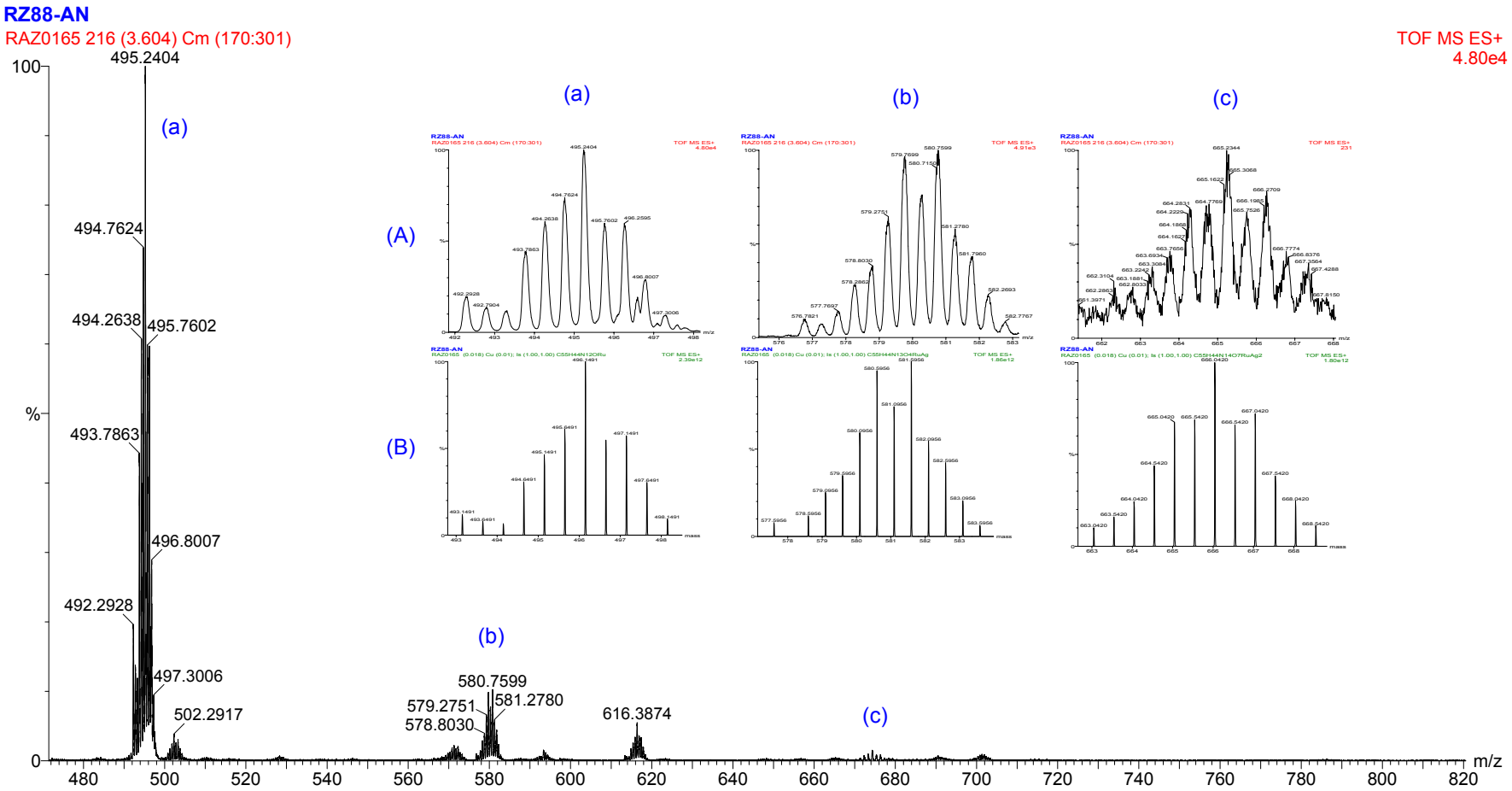

Fig. V. ES-MS of the product obtained from the reaction of $[Ru(pzt)(ttp)](PF_6)_2$ complex with Ag NO_3 in acetone. (A) High resolution scans of the three signals (a), (b), and (c); (B) Calculated isotope distribution patterns for (a) $[Ru(pzt)(ttp)]^{2+}$,(b) $[Ru(pzt)(ttp)Ag(NO_3)]^{2+}$, and (c) $[Ru(pzt)(ttp)Ag_2(NO_3)_2]^{2+}$.

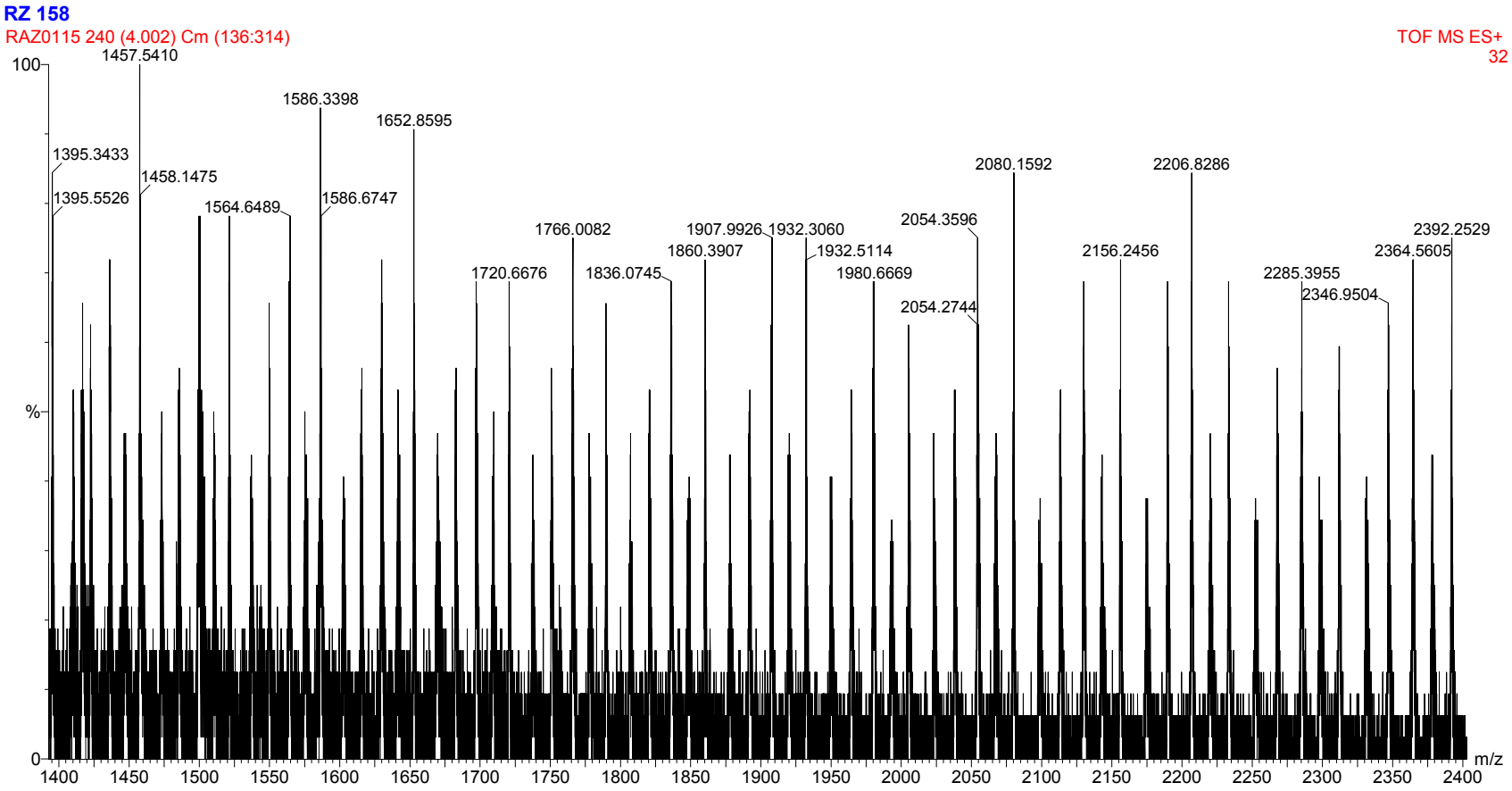

Fig. VI. Expanded region (*m/z* 1400 to 2400) of ES-MS data for the material formed in the reaction of $[Fe(pzt)_2](PF_6)_2$ with $AgNO_3$ in acetone.

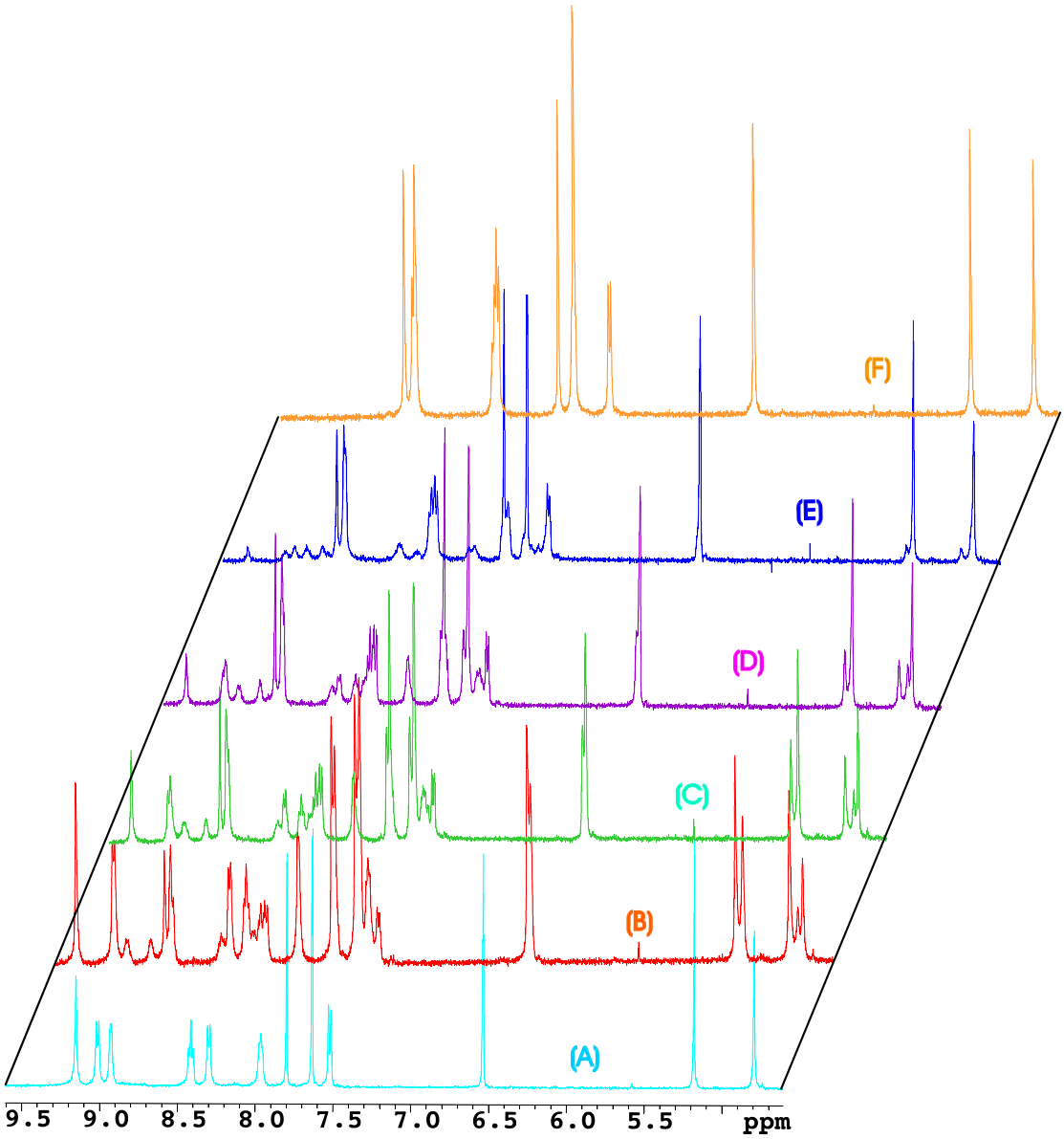

Fig. VII. ^{1}NMR titration of [Zn(pzt)Cl_3] in dmso-d_6 with $AgBF_4$ solution in dmso-d_6.

(A) [Zn(pzt)Cl_3] in dmso-d_6

(B) [Zn(pzt)Cl_3] + $AgBF_4$ in dmso-d_6 (1:3)

(C) [Zn(pzt)Cl_3] + $AgBF_4$ in dmso-d_6 (1:5)

(D) [Zn(pzt)Cl_3] + $AgBF_4$ in dmso-d_6 (1:7)

(E) [Zn(pzt)Cl_3] + $AgBF_4$ in dmso-d_6 (1:11)

(F) [Zn(pzt)Cl_3] + $AgBF_4$ in dmso-d_6 (1:20)

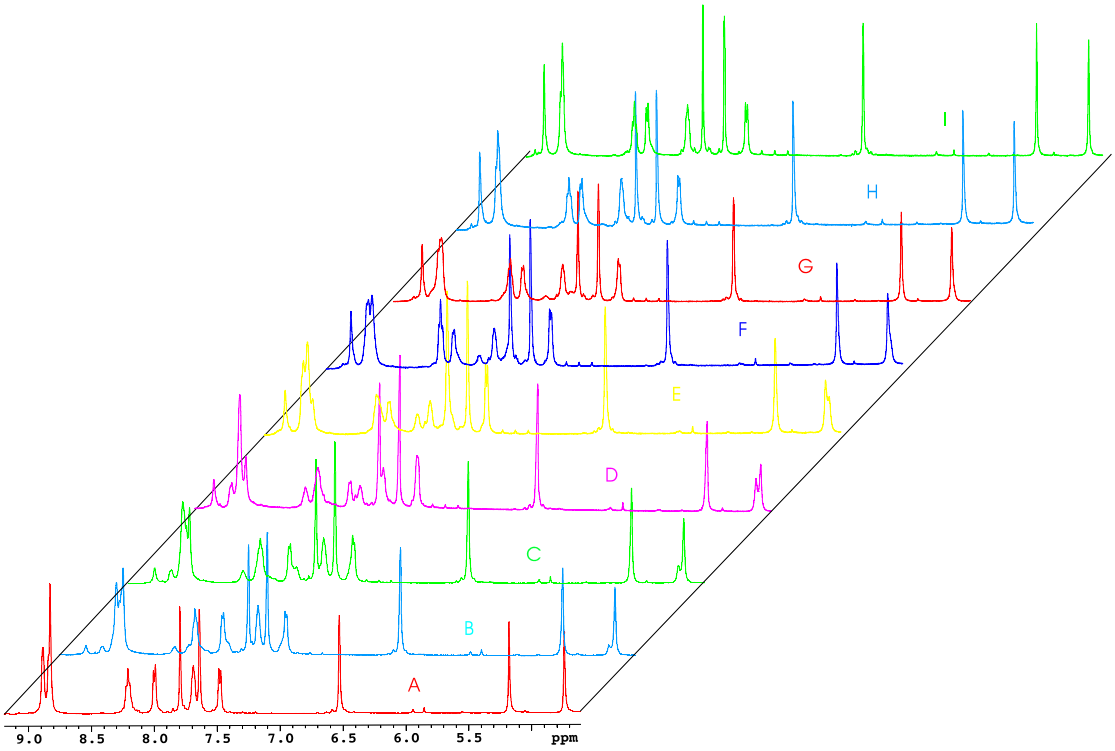

Fig. VIII ^{1}NMR titration of pzt ligand in dmso-d_6 with $ZnCl_2$ solution in dmso-d_6.

A ^{1}NMR of pzt ligand in dmso-d_6.

E ^{1}NMR of pzt + $ZnCl_2$ in dmso-d_6 (L:M)(1:0.5).

I ^{1}NMR of [Zn(pzt)Cl_2] complex in dmso-d_6 (L:M)(1:1)

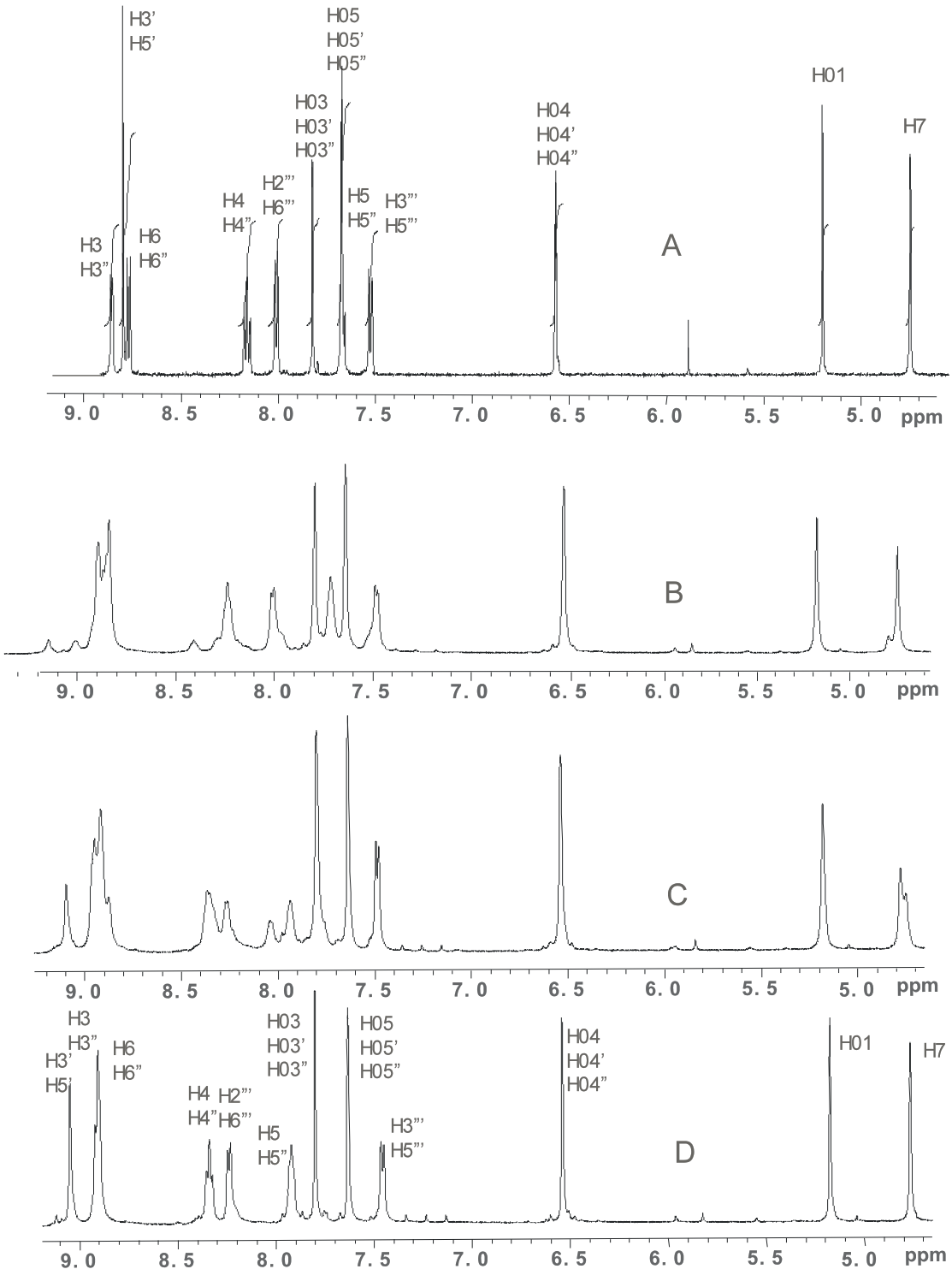

Fig. IX ^{1}NMR titration of pzt ligand in dmso-d_6 with $ZnCl_2$ solution in dmso-d_6.

A ^{1}NMR of pzt ligand in dmso-d_6.

B ^{1}NMR of pzt + $ZnCl_2$ in dmso-d_6 (L:M)(1:0.1).

C ^{1}NMR of pzt + $ZnCl_2$ in dmso-d_6 (L:M)(1:0.5).

D ^{1}NMR of [Zn(pzt)Cl_2] complex in dmso-d_6 (L:M)(1:1)