Solvation effects on the stability of Silver(I) complexes with pyridine-containing ligands studied by thermodynamic and DFT methods.

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Supplementary Information

Figure S1 Optimized geometry of dmso.

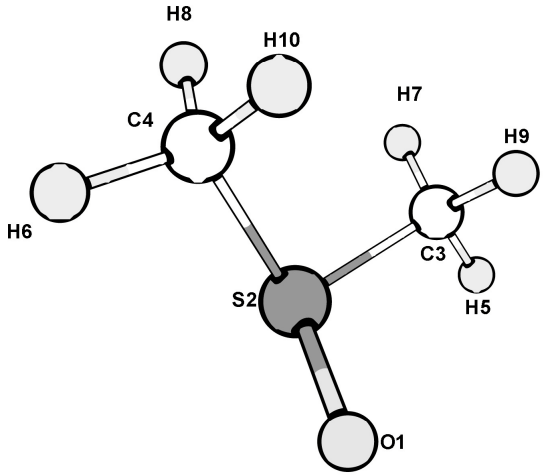

Table S1 Geometrical parameters table for dmso (point group C_s)

R(1-2)	1.520 A(1-2-3)	106.6 A(5-3-7)	110.1
R(2-3)	1.837 A(2-3-5)	106.2 A(5-3-9)	109.7
R(3-5)	1.091 A(2-3-7)	110.2 A(7-3-9)	111.4
R(3-7)	1.094 A(2-3-9)	109.1	
R(3-9)	1.094 A(3-2-4)	97.2	

Figure S2 Optimized geometry of pyridine.

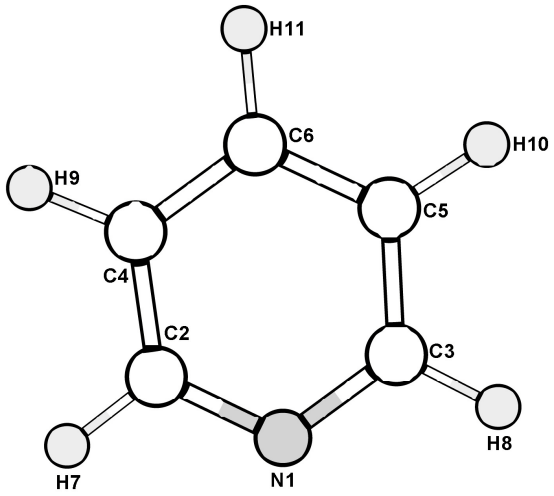

Table S2 Geometrical parameters table for pyridine (C_{2v}).

R(1-2)	1.341	A(1-2-4)	123.7	A(4-6-5)	118.5
R(2-4)	1.398	A(1-2-7)	115.9	A(4-6-11)	120.8
R(2-7)	1.089	A(2-1-3)	117.2	A(6-4-9)	121.3
R(4-6)	1.396	A(2-4-6)	118.5		
R(4-9)	1.086	A(2-4-9)	120.2		
R(6-11)	1.087	A(4-2-7)	120.4		

Figure S3 Optimized geometry of $[Agpy]^+$ (C_{2v}).

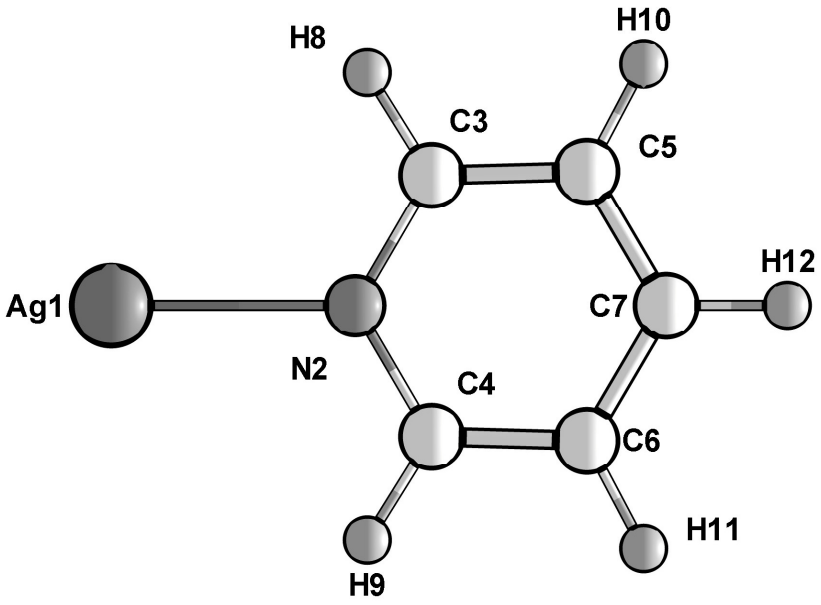

Table S3 Geometrical parameters table for $[Agpy]^+$ (C_{2v}).

R(1-2)	2.186	A(1-2-3)	120.4	A(5-7-6)	118.8
R(2-3)	1.352	A(2-3-5)	122.0	A(5-7-12)	120.6
R(3-5)	1.391	A(2-3-8)	117.5	A(7-5-10)	121.4
R(3-8)	1.086	A(3-2-4)	119.1		
R(5-7)	1.397	A(3-5-7)	119.1		
R(5-10)	1.085	A(3-5-10)	119.5		
R(7-12)	1.086	A(5-3-8)	120.6		

Table S4 Thermodynamic functions for the reaction $Ag^+ + jL \rightleftharpoons AgL_j^+$ in dmso at 298 K and I = 0.1 mol dm^{-3} (L =amine). n-but = N-butylamine, en = ethylenediamine; dien = diethylenetriamine.

Amine	Complex	Logβ	$-\Delta G°$ (kJ mol^{-1})	$-\Delta H°$ (kJ mol^{-1})	$-T\Delta S°$ (kJ mol^{-1})
n-but[a]	AgL^+	3.58	20.4	31.4	11
	AgL_2^+	7.34	41.9	71.5	29.6
en[b]	AgL^+	5.34	30.5	63	32.5
	AgL_2^+	9.50	54.2	85	30.8
dien[b]	AgL^+	7.46	42.6	78.2	35.6
	AgL_2^+	10.20	58.2	94	35.8

[a] ref. 9a ; [b] ref 9b

Table S5 Calculated Mulliken Charges for the silver complexes (Numbering Scheme of Figure 2)

$[Ag(dmso)_3py]^+$		$[Ag(dmso)_3]^+$		$[Ag(H_2O)_3py]^+$		$[Ag(H_2O)_3]^+$	
Ag	0.518	Ag	0.572	Ag	0.541	Ag	0.710
O1	-0.704	O1	-0.698	O1	-0.718	O1	-0.723
O2	-0.707	O2	-0.696	O2	-0.731	O2	-0.715
S3	0.760	S3	0.758	N3	0.051		
S4	0.702	S4	0.758	C4	-0.250		
N8	0.155			C5	0.207		
C9	-0.382			C6	-0.392		
C10	0.344						
C11	-0.565						

Figure S4 NMR (aromatics) spectra of dmso solutions of: a) amp ; b) R_c = 0.8.

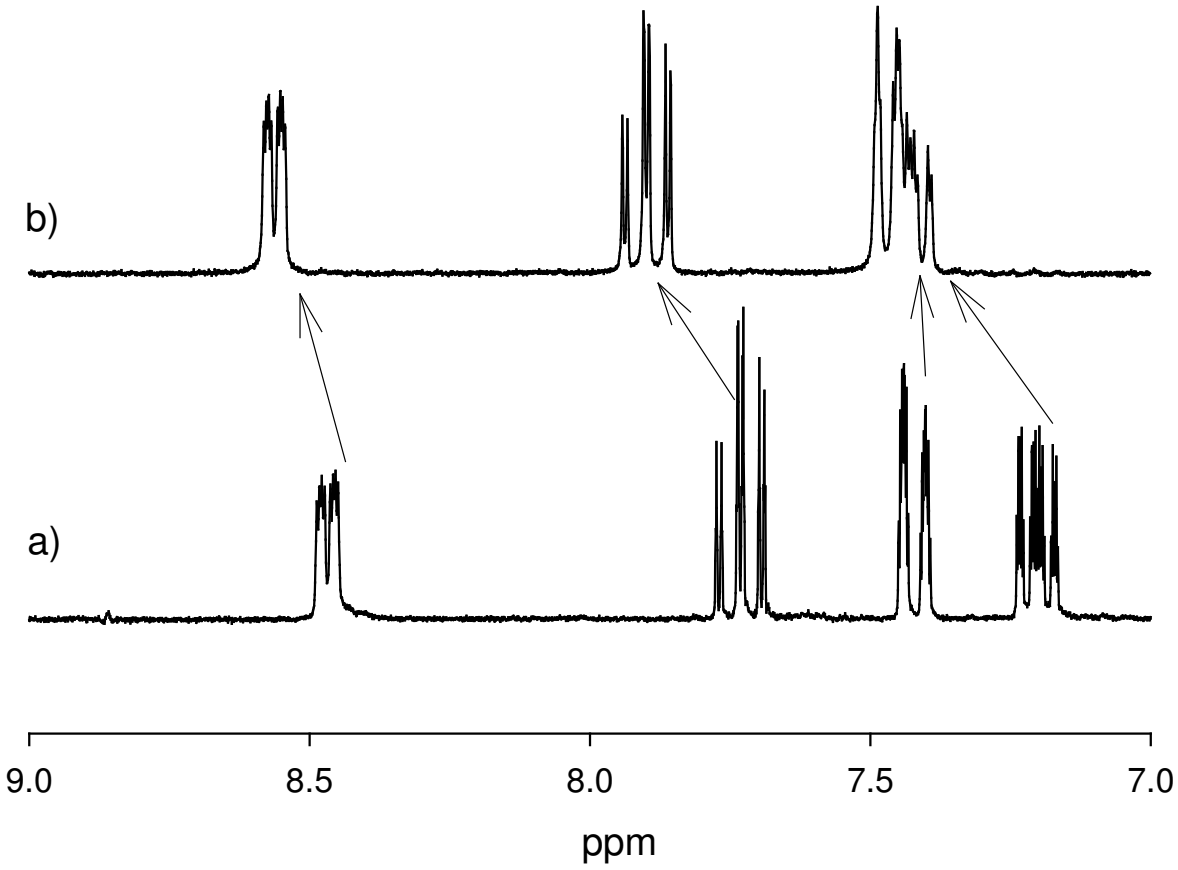

Figure S5 NMR spectra of dmso solutions at different R_c values. a) dpa ; b) $R_c=1$; c) $R_c=1.5$. This last value was used in order to avoid the presence of free ligand.