

CHAPTER V

Complexes of Silver(I) with Protonated Aminomethylpyridines

Complexes formed with cationic ligands are much less numerous than anionic or neutral ligands. Examples of structurally characterized metal complexes belong to four categories: (i) the well known tropylium cation,¹ (ii) thiamine substituted ligands,² (iii) the quaternary ammonium ion, $N(CH_2CH_2)_3NH^+$,³ and (iv) the protonated phosphinoalkyl amine $(Ph_2PCH_2CH_2)_3NH^+$.⁴ Protonation of the primary amine side chain of an N-heterocyclic ligand leads to another class of such ligands. The ligand aminomethylpyridine (amp) provides an example for this class of ligands, where the amino side chain can be protonated and still it can complex to metal ions through the pyridine N atom. Existence of $pmaH^+$ has been observed in the solution studies of Ag/amp systems⁵ and its crystallographic characterization as $Ag(2-pmaH)_2(NO_3)_3$ ⁶ has been recently reported from our laboratory. Complexes of these ligands are expected to have added stability due to hydrogen bonding with anions. Continuing with the above protonated system, our efforts with polymeric Ag(I) complexes of 3-amp and 4-amp have resulted in the isolation of two more protonated amp systems, whose structural details are presented in this chapter.

5.1. Experimental

5.1.1. Synthesis

(a) Preparation of $\text{Ag}_2(3\text{-pmaH})_3(\text{OH}_2)(\text{ClO}_4)_5$ (1): Compound 1 was synthesized as follows. Polymeric $\text{Ag}(3\text{-amp})\text{ClO}_4^7$ (0.830g, 2.63 mmol) was dissolved in 40 mL 0.1N HClO_4 and concentrated on a water bath until the final volume reduced to half the initial. The solution was then filtered and desiccated, which yielded white crystalline material after about 10 days. Recrystallization of the crystalline material from 10 mL 0.1N HClO_4 at 4 °C gave suitable single crystals for X-ray analysis. Yield: 0.485g (0.46 mmol, 52 %). Anal. Calcd. for $\text{C}_{18}\text{H}_{29}\text{N}_6\text{O}_{21}\text{Cl}_5\text{Ag}_2$ (MW: 1058.46) C, 20.43; H, 2.76; N, 7.94. Found, C, 23.49; H, 2.74, N, 8.21. Characteristic IR peaks ($\text{KBr}/\text{cm}^{-1}$): 3072(br), 1606(w), 1389(w), 1074(br), 860(s), 806(s), 708(s), 673(s), 629(s).

(b) Preparation of $\text{Ag}_2(4\text{-pmaH})_4(\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ (2): Compound 2 was obtained as detailed. Polymeric $\text{Ag}(4\text{-amp})\text{ClO}_4^7$ (0.500g, 1.55 mmol) was dissolved in 30 mL 0.1N HClO_4 and concentrated on a water bath until the final volume reduced to half the initial. The solution was then filtered and desiccated which yielded white crystalline material after about 10 days. Recrystallization of the crystalline material from 10 mL 0.1N HClO_4 at 4 °C gave single crystals suitable for X-ray analysis. Yield: 0.410g (0.32 mmol, 82 %). Anal. Calcd. for $\text{C}_{18}\text{H}_{29}\text{N}_6\text{O}_{21}\text{Cl}_5\text{Ag}_2$ (MW: 1285.08) C, 22.43; H, 3.14; N, 8.72. Found, C, 21.72; H, 3.08; N, 7.87. Characteristic IR peaks ($\text{KBr}/\text{cm}^{-1}$): 3052(br), 1615(w), 1501(w), 1391(w), 1088(br), 774(w), 625(s).

(c) Attempted Preparation of $\text{Ag}(2\text{-pmaH})_2(\text{ClO}_4)_3$ (3): Compound 3 was attempted to prepare following the procedure adopted for 1 and 2. When a solution of polymeric $\text{Ag}(2\text{-amp})\text{ClO}_4^7$ in 0.1N HClO_4 is evaporated, white crystalline material is obtained. Repeated recrystallization of the crystalline material at 4 °C always gave

crystalline solid only. When the recrystallization is tried at RT, colorless single crystals are obtained. On the basis of C, H, N analysis and absence of silver in the crystals they are confirmed as NH_4ClO_4 . Anal. Calcd. for $\text{H}_4\text{NO}_4\text{Cl}$ (MW: 117.49) H, 3.43; N, 11.92. Found, H, 3.05; N, 10.51.

5.1.2. Physical Measurements: IR spectra were recorded on a Jasco 5300 FT/IR infrared spectrometer. C, H, N analysis was performed on a Perkin-Elmer 240C elemental analyzer. X-ray data were collected on an Enraf Nonius CAD-4 diffractometer.

5.1.3. X-ray Crystallography: X-ray data were collected for colorless crystals of 1 with dimensions 0.56 x 0.38 x 0.30 mm and of 2 with dimensions 0.44 x 0.44 x 0.32 mm on an Enraf Nonius CAD-4 diffractometer using graphite monochromated $\text{Mo-K}\alpha$ radiation. The data were corrected for Lorentz polarization effects and absorption.⁸ The structures were solved by a combination of Patterson heavy atom method and direct methods (SHELXS) and refined (over F^2) by least squares techniques (SHELXL).⁹ Drawings were made using ORTEP-III.¹⁰

1 crystallizes in the triclinic system, space group $P1$, with 2 molecules in the unit cell. A total of 4610 reflections (4532 unique, 3740 with $F > 4\sigma F$) were collected in the θ range 1.94 to 24.93, with indices $-2 < h < 10$, $-12 < k < 13$, $-19 < l < 18$. The collected data is only 76% of the total data, as some of the data could not be collected due to instrumental problem. All the non-hydrogen atoms were refined anisotropically while the ring hydrogen atoms were included in the calculated positions using a riding model. Bond length constraints were applied to water and ammonio hydrogens. All hydrogens were assigned fixed U_{iso} values, equal to $1.2U_{eq}$ of the parent atom for ring atoms and $1.5U_{eq}$ for CH_2 , NH_3^+ and H_2O hydrogen atoms. The final cycle of full matrix least squares refinement on F^2 converged with unweighted and weighted refinement factors of $R1 = 0.0388$ and $wR2 = 0.0949$ respectively. The goodness of the fit (S) is 1.032 for 4532 unique reflections and 499

parameters. The maximum and minimum residual electron density on the final fourier map corresponded to 0.700 and -0.973 e/A³ respectively.

2 crystallizes in the triclinic system, space group $P\bar{1}$, with 2 molecules in the unit cell. A total of 8140 reflections (7941 unique, 5117 with $F > 4\sigma F$) were collected in the θ range 1.82 to 25.03, with indices $-4 < h < 13$, $-16 < k \leq 17$, $-17 < l < 17$. All the non-hydrogen atoms were refined anisotropically while the ring hydrogen atoms and ammonio hydrogen atoms were included in the calculated positions using a riding model. The U_{iso} values for ammonio hydrogen atoms were refined. Water hydrogens were located from difference maps and bond length constraints were applied. Except ammonio hydrogens, all hydrogens were assigned fixed U_{iso} values, equal to $1.2U_{eq}$ of the parent ring atoms and $1.5U_{eq}$ for CH₂ and H₂O hydrogen atoms. Ammonio group hydrogen thermal parameters were refined. The perchlorate oxygens were found to be disordered. The disorder is modeled by splitting each oxygen into two halves, which were refined isotropically by free variable (FVAR) refinement. The final cycle of full matrix least squares refinement on F^2 converged with unweighted and weighted refinement factors of $R = 0.0628$ and $wR2 = 0.1617$ respectively. The goodness of fit (S) = 1.044 for 7939 unique reflections and 605 parameters. The maximum and minimum residual electron density on the final fourier map corresponded to 0.780 and -0.582 e/A³ respectively.

Crystallographic data for 1 and 2 are presented in Table 5.1, and atomic parameters for 1 are tabulated in Table 5.2, and for 2 in Table 5.3 respectively.

Table 5.1 Crystallographic data for $\text{Ag}_2(3\text{-pmaH})_3(\text{OH}_2)(\text{ClO}_4)_5$ (1) and $\text{Ag}_2(4\text{-pmaH})_4(\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ (2).

	1	2
formula	$\text{C}_{18}\text{H}_{29}\text{Ag}_2\text{Cl}_5\text{N}_6\text{O}_{21}$	$\text{C}_{24}\text{H}_{40}\text{Ag}_2\text{Cl}_6\text{N}_8\text{O}_{26}$
formula weight	1058.46	1285.08
a (Å)	9.6868(7)	11.3358(7)
b (Å)	11.4840(8)	14.5436(10)
c (Å)	17.0637(13)	14.6015(17)
α (°)	102.288(6)	77.700(8)
β (°)	100.965(8)	89.519(6)
γ (°)	107.214(5)	74.421(6)
V (Å ³)	1705.2(2)	2262.5(3)
Z	2	2
Space group	$P\bar{1}$	$P\bar{1}$
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
ρ_{calcd} (Mg/m ³)	2.061	1.886
μ (mm ⁻¹)	1.634	1.316
$R1$	0.0388	0.0628
$wR2$	0.0949	0.1617

weighting scheme, **1**: $A = 0.0510$; $B = 4.3726$; **2**: $A = 0.1016$; $B = 1.3280$ (see p. vi for definitions).

Table 5.2 Atomic parameters for $\text{Ag}_2(\text{3-pmaH})_3(\text{OH}_2)(\text{ClO}_4)_5$ (1).

Atom	10^4x	10^4y	10^4z	10^3U_{eq}	Atom	10^4x	10^4y	10^4z	10^3U_{eq}
Ag1	2311(1)	4952(1)	1365(1)	57(1)	OW	-121(7)	5708(7)	6351(5)	136(3)
N1	4711(5)	5649(4)	1864(3)	40(1)	CH	-3668(2)	1612(1)	2256(1)	41(1)
Cl	5479(6)	6887(5)	2253(3)	39(1)	01	-4451(5)	1777(4)	1513(3)	57(1)
C2	6987(5)	7353(5)	2663(3)	32(1)	02	-2177(5)	1700(5)	2231(3)	79(2)
C3	7744(6)	6512(5)	2665(3)	40(1)	03	-4463(6)	392(4)	2329(3)	71(1)
C4	6966(6)	5246(5)	2252(3)	42(1)	04	-3607(4)	2570(4)	2975(3)	54(1)
C5	5461(6)	4845(5)	1874(3)	41(1)	Cl2	1356(2)	8150(1)	5162(1)	49(1)
C6	7753(6)	8749(5)	3117(3)	40(1)	05	2887(5)	8896(5)	5380(3)	73(1)
N2	8594(5)	9468(4)	2628(3)	41(1)	06	1187(9)	6856(5)	4872(5)	130(3)
N3	-91(5)	4176(4)	849(3)	38(1)	07	784(5)	8328(4)	5861(3)	74(1)
C7	-763(6)	2907(5)	549(3)	36(1)	08	605(7)	8468(9)	4528(4)	140(3)
C8	-2257(5)	2329(5)	122(3)	32(1)	Cl3	2188(2)	7935(1)	2681(1)	39(1)
C9	-3106(6)	3098(5)	28(3)	42(1)	09	3627(4)	8511(4)	3278(2)	52(1)
Cl0	-2415(7)	4397(5)	354(4)	45(1)	O10	2383(5)	7714(4)	1859(2)	55(1)
Cl1	-934(6)	4891(5)	754(3)	41(1)	O11	1396(5)	6757(4)	2795(3)	68(1)
Cl2	-2948(7)	907(5)	-206(4)	51(2)	012	1379(5)	8791(4)	2783(3)	70(1)
N4	-2370(6)	386(4)	-899(3)	46(1)	Cl4	2212(2)	1999(1)	-434(1)	46(1)
Ag2	1551(1)	5163(1)	5799(1)	88(1)	013	1114(5)	2179(4)	-1025(3)	61(1)
N5	3303(5)	4378(4)	5629(3)	43(1)	014	3004(4)	1301(4)	-847(3)	52(1)
Cl3	3015(6)	3202(5)	5136(3)	42(1)	015	1443(8)	1259(6)	30(4)	110(2)
Cl4	4085(6)	2644(5)	5110(3)	35(1)	016	3225(7)	3187(5)	94(4)	118(3)
Cl5	5516(7)	3333(6)	5614(4)	48(2)	Cl5	1573(1)	2014(1)	2362(1)	36(1)
Cl6	5819(7)	4544(6)	6111(4)	55(2)	017	1422(5)	3183(4)	2287(3)	65(1)
Cl7	4718(5)	5013(4)	6106(3)	46(2)	018	3052(5)	2038(5)	2355(3)	71(1)
Cl8	3661(5)	1295(4)	4577(3)	50(2)	019	501(4)	973(4)	1698(2)	53(1)
N6	4298(6)	1243(4)	3841(3)	44(1)	O20	1335(5)	1851(4)	3140(2)	59(1)

Table 5.3 Atomic parameters for $\text{Ag}_2(4\text{-pmaH})_4(\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ (2).

Atom	10^4x	10^4y	10^4z	10^3U_{eq}	Atom	10^4x	10^4y	10^4z	10^3U_{eq}
Ag1	0	5000	5000	85(1)	O5B(0.30)	-5440(3)	5260(3)	3380(2)	118(10)
N1	-1868(5)	5931(4)	4932(3)	51(1)	O6A(0.70)	-4644(9)	6384(7)	2055(9)	79(3)
N2	-5952(5)	7920(4)	3451(4)	54(1)	O6B(0.30)	-4642(15)	6479(12)	2401(15)	49(5)
Cl	-2098(6)	6888(5)	4779(5)	54(2)	O7A(0.70)	-5288(9)	4995(8)	2023(6)	67(3)
C2	-3247(6)	7497(5)	4629(5)	52(2)	O7B(0.30)	-5575(19)	5392(19)	1814(15)	65(6)
C3	-4253(5)	7137(4)	4639(4)	41(1)	O8A(0.70)	-3802(9)	4848(7)	3188(9)	82(3)
C4	-4002(6)	6134(5)	4860(5)	54(2)	O8B(0.30)	-3573(17)	4942(13)	2721(17)	67(6)
C5	-2846(7)	5551(5)	4995(5)	54(2)	Cl3	2414(2)	819(1)	3583(1)	62(1)
C6	-5534(6)	7794(6)	4425(5)	67(2)	O9A(0.65)	2700(7)	1593(6)	2968(6)	70(3)
Ag2	3817(1)	3340(1)	2858(1)	84(1)	O9B(0.35)	1389(15)	1261(12)	2779(11)	78(5)
N3	1989(5)	4269(5)	2766(4)	57(2)	O10A(0.65)	1606(10)	1171(7)	4278(7)	96(3)
N4	-2177(5)	6323(4)	1630(4)	51(1)	O10B(0.35)	3410(2)	149(16)	3227(16)	119(8)
N5	5591(5)	2322(4)	3040(4)	58(2)	O11A(0.65)	2130(12)	141(9)	3247(10)	122(4)
N6	9544(5)	-253(4)	2973(4)	52(1)	O11B(0.35)	2740(2)	1311(18)	4056(17)	126(8)
Cl	1759(6)	5237(5)	2594(5)	60(2)	O12A(0.65)	3546(13)	339(11)	4199(10)	139(5)
C8	618(6)	5853(5)	2549(5)	49(2)	O12B(0.35)	2070(2)	-32(16)	4044(16)	112(7)
C9	-380(5)	5469(4)	2685(4)	40(1)	Cl4	1691(2)	8594(1)	1306(1)	55(1)
ClO	-150(6)	4466(5)	2891(5)	55(2)	O13A(0.65)	1958(10)	9045(6)	2057(7)	55(3)
CH	1018(7)	3896(5)	2913(5)	65(2)	O13B(0.35)	2360(3)	8980(17)	1824(19)	98(8)
C12	-1657(5)	6129(5)	2604(4)	51(2)	O14A(0.65)	371(10)	8758(10)	1312(10)	78(3)
C13	5707(6)	1377(6)	3386(6)	67(2)	O14B(0.35)	533(18)	8461(18)	1625(17)	75(6)
C14	6818(7)	703(5)	3619(5)	61(2)	O15A(0.65)	1989(13)	9086(9)	439(7)	81(4)
C15	7883(5)	972(5)	3490(4)	44(1)	O15B(0.35)	1440(2)	9420(17)	438(13)	81(7)
C16	7738(6)	1949(5)	3101(6)	64(2)	O16A(0.65)	2415(12)	7583(9)	1533(12)	99(4)
C17	6616(7)	2595(5)	2898(6)	72(2)	O16B(0.35)	2100(2)	7689(15)	1070(2)	91(8)
C18	9100(6)	267(6)	3747(5)	62(2)	Cl5	3378(2)	1020(1)	-2001(1)	60(1)
Ag3	5000	5000	0	76(1)	O17A(0.57)	2343(11)	1343(8)	-2700(10)	74(4)
N7	5531(5)	6334(4)	-334(4)	53(1)	O17B(0.43)	2172(14)	1398(11)	-2371(13)	69(5)
N8	7872(7)	8923(5)	-1006(6)	85(2)	O18A(0.57)	4351(17)	537(15)	-2508(13)	119(7)
C19	6617(7)	6359(5)	-657(4)	55(2)	O18B(0.43)	4369(17)	883(16)	-2595(13)	85(6)
C20	7009(6)	7200(5)	-859(4)	49(2)	O19A(0.57)	3304(12)	112(11)	-1447(10)	104(5)
C21	6243(6)	8057(4)	-709(4)	44(1)	O19B(0.43)	3476(18)	452(16)	-1109(16)	116(7)
C22	5100(7)	8036(5)	-383(5)	61(2)	O20A(0.57)	3497(12)	1681(9)	-1455(10)	98(5)
C23	4787(7)	7166(5)	-199(5)	62(2)	O20B(0.43)	3881(15)	1868(11)	-2026(13)	91(6)

Table 5.3 contd.

C24	6569(7)	9014(5)	-892(5)	65(2)	C16	1358(3)	6194(2)	-734(2)	97(1)
CH	1181(2)	7403(1)	4498(2)	65(1)	O21A(0.57)	198(16)	6839(12)	-1196(12)	116(6)
O1A(0.66)	1423(7)	8316(6)	4499(7)	66(2)	O21B(0.43)	600(3)	5470(2)	-540(18)	174(11)
O1B(0.34)	1549(17)	8186(14)	4023(15)	85(6)	O22A(0.57)	2212(12)	5595(9)	-1234(8)	87(4)
O2A(0.66)	151(8)	7624(6)	3788(6)	72(3)	O22B(0.43)	1630(3)	5299(16)	-944(16)	131(8)
O2B(0.34)	690(2)	6773(17)	4190(15)	111(8)	O23A(0.57)	1120(15)	6023(11)	224(11)	125(6)
O3A(0.66)	2209(9)	6831(7)	4053(7)	94(3)	O23B(0.43)	1830(2)	6254(16)	114(16)	136(8)
O3B(0.34)	2340(2)	6772(16)	5149(16)	116(8)	O24A(0.57)	2194(16)	6876(13)	-824(12)	159(7)
O4A(0.66)	955(9)	6849(8)	5284(7)	98(4)	O24B(0.43)	593(19)	6965(14)	-1439(14)	97(6)
O4B(0.34)	350(2)	7767(18)	5284(16)	120(8)	OW1	9206(5)	7545(5)	596(4)	73(2)
C12	-4857(2)	5517(1)	2608(1)	60(1)	OW2	9463(5)	1054(4)	1235(4)	75(2)
O5A(0.70)	-5775(7)	5832(7)	3268(5)	57(3)					

The site occupation factors of disordered sites are given after the respective atom labels.

5.2. Results and Discussion

5.2.1. Synthesis: The C,H,N analysis results do not correspond to the given formula for 1. Repeated analysis results always matched with a formula $\text{Ag}(3\text{-pmaH})_2(\text{ClO}_4)_3$ as opposed to the formula corresponding to 1. This might be due to the fact, that the bulk sample corresponds to the formula, $\text{Ag}(3\text{-pmaH})_2(\text{ClO}_4)_3$, while a minor fraction corresponds $\text{Ag}_2(3\text{-pmaH})_3\text{OH}_2(\text{ClO}_4)_5$, which has two protonated ligands around Ag1 and one protonated ligand and one water molecule around Ag2. The single crystal chosen for X-ray measurements probably is the one corresponding to a minor fraction of the sample.

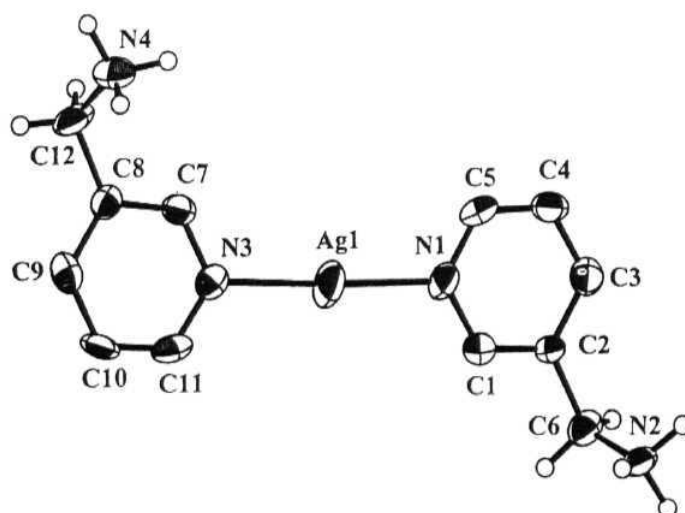
5.2.2. Structure of $\text{Ag}_2(3\text{-pmaH})_3(\text{OH}_2)(\text{ClO}_4)_5$ (1): The asymmetric unit of 1 contains two silver centers, viz., $[\text{Ag}(3\text{-pmaH})_2]^{3+}$ and $[\text{Ag}(3\text{-pmaH})(\text{OH}_2)]^{2+}$ (Figure 5.1). The coordination environment of Ag1 and Ag2 are shown in Figure 5.1 (a) and (b) respectively. Ag1 is coordinated to two protonated ligands and has a linear

geometry. Ag2 is coordinated to one protonated ligand and one water molecule. Bond lengths and angles are presented in Table 5.4. The geometry around Ag2 is bent. The

Table 5.4 Bond lengths (Å) and angles (°) for $\text{Ag}_2(3\text{-pmaH})_3(\text{OH}_2)(\text{ClO}_4)_5$ (1).

Ag1-N1	2.150(4)	Ag1-N3	2.155(4)	N1-Ag1-N3	177.66(16)
Ag2-N5	2.182(4)	Ag2-OW	2.198(6)	N5-Ag2-OW	160.0(3)

geometry around Ag1 is more linear than in the previously reported $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$,⁶ while the coordination geometry of Ag2 is similar to that of $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$. The bent geometry around Ag2 in 1 could be attributed to the coordination of OH_2 to Ag2, which is involved in hydrogen bonding with the anions, whereas, in the previous case of $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$, the bent geometry around Ag was attributed to the coordination of NO_3^- oxygen to Ag. Comparing with the geometry of $\text{Ag}(3\text{-pmaH})_2^{3+}$ in the same crystal, it is seen that coordination by OH_2



(a)

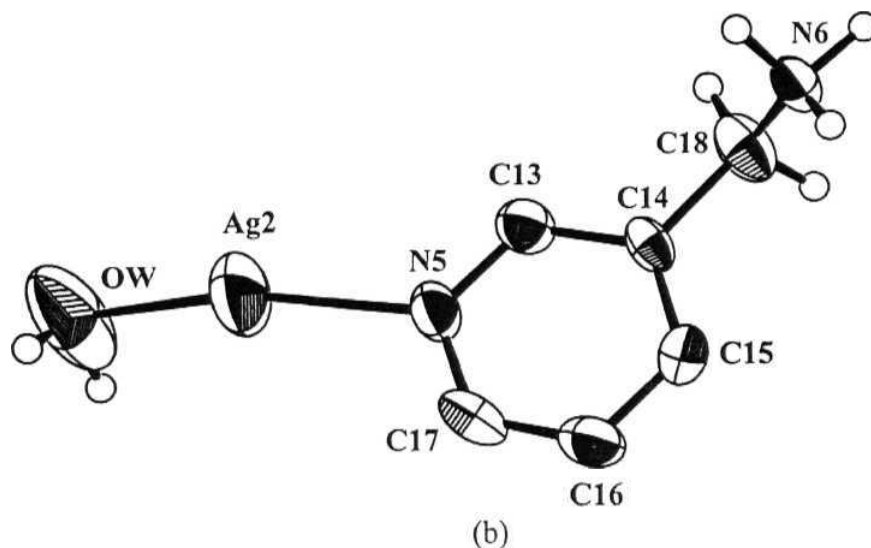


Figure 5.1 Ortep view of the cationic units in 1. (a) coordination environment of Ag1 and (b) coordination environment of Ag2 with atom labeling. Atoms are drawn as 50% probability ellipsoids. Anions and ring hydrogens are omitted for clarity.

has caused a lengthening of the *trans* Ag-N bond [$\text{Ag2-N5} = 2.182(4) \text{ \AA}$ while $\text{Ag1-N1} = 2.150(4) \text{ \AA}$ and $\text{Ag1-N3} = 2.155(4) \text{ \AA}$], Complexes where there is a direct coordination between water oxygen and silver are much less in number, compared to those with other donor atoms. In such complexes Ag is found to be with 3-coordination,¹¹⁻¹⁷ 4-coordination¹⁸⁻²⁰ or 5-coordination.²⁰²⁴ Two coordinate Ag with one water ligand is found only in $[\text{Ag}_2(\text{dbpe})(\text{H}_2\text{O})_2](\text{BF}_4)_2$ ²⁵ in which the coordination is more linear [$\text{P-Ag-O} = 169.8(1)^\circ$], than in 1. It has been proposed that the *trans* influence of the water ligand causes a shortening (0.06 Å) of the Ag-P bond in this structure. This is in contrast to what is observed in 1, where a lengthening (0.03 Å) of the Ag2-N5 bond is seen. Both linear and bifurcated 3 center hydrogen

bonds are found in 1, with $H\cdots A$ distances in the range 1.99 (3) Å - 2.57 (5) Å (Figure 5.2, Table 5.4).

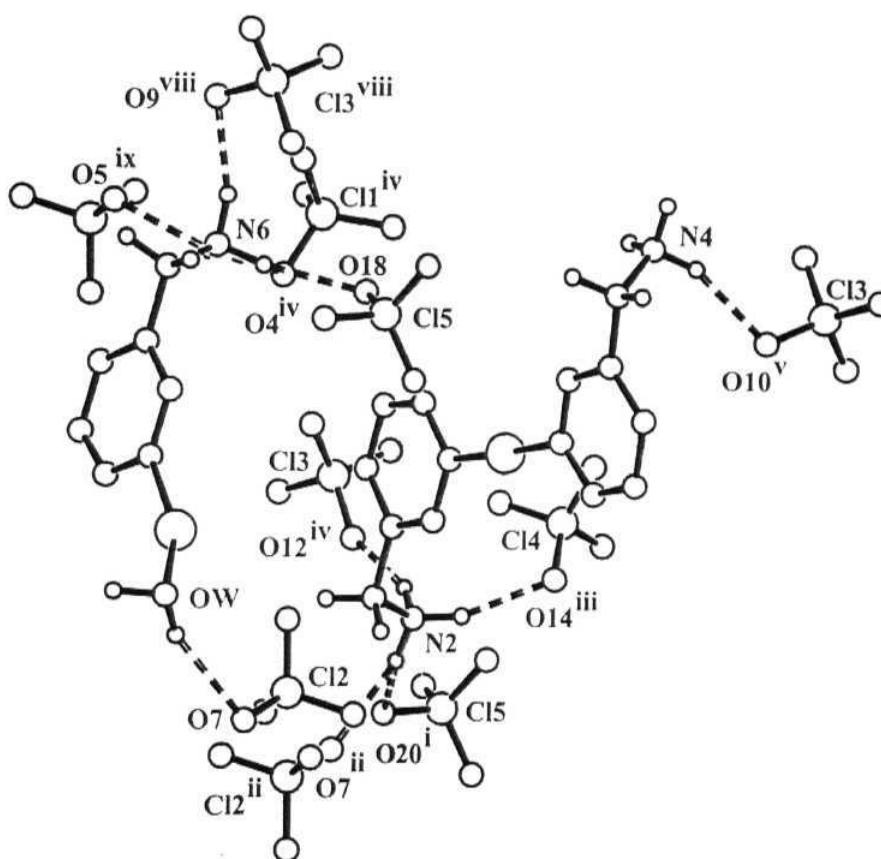


Figure 5.2 View of the hydrogen bonding (broken lines) present in 1. Only important hydrogen bonds are shown. Symmetry codes: (i) $x + 1, y + 1, z$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $v + 1, y, z$; (v) $-x, -y + 1, -z$; (viii) $x, y - 1, z$; (ix) $-x + 1, -y + 1, -z + 1$.

It appears from Figure 5.2 that hydrogen bonding has an influence on the coordination geometry around Ag_2 in the aquo complex. Such influence of weak

interactions within the crystal lattice on the coordination geometry of Ag(I) complexes has been reported before.²⁶

Table 5.4 Hydrogen bonding in $\text{Ag}_2(3\text{-pmaH})_3(\text{OH}_2)(\text{ClO}_4)_5$ (1).

D-H...A	d(A)	D(A)	$\theta(^{\circ})$	D-H...A	d(A)	D(A)	$G(^{\circ})$
N2-HN21...O20#1	2.19(4)	3.017(6)	142(5)	N4-HN43...O15	2.53(3)	3.473(9)	166(5)
N2-HN21...O7#2	2.25(4)	3.025(6)	136(5)	N6-HN61...O9#8	1.96(3)	2.908(6)	162(5)
N2-HN22...O14#3	1.99(3)	2.945(6)	162(5)	N6-HN61...O12#8	2.57(5)	3.220(7)	123(4)
N2-HN23...O12#4	2.07(3)	3.002(6)	160(5)	N6-HN62...O4#4	2.25(5)	2.982(6)	131(5)
N2-HN23...O13#3	2.58(6)	3.090(6)	113(4)	N6-HN62...O5#9	2.26(5)	2.863(7)	119(4)
N4-HN41...O10#5	2.06(3)	2.995(6)	158(5)	N6-HN63...O18	2.06(2)	3.032(7)	169(5)
N4-HN42...O18#6	2.31(4)	3.115(7)	139(5)	N6-HN63...O20	2.52(5)	3.224(7)	129(5)
N4-HN42...O1#7	2.40(5)	3.145(7)	133(5)	OW-HW1...O7	2.28(6)	3.211(11)	156(12)
N4-HN43...O19#6	2.52(6)	3.046(6)	114(4)				

#1 $x + 1, y + 1, z$	#2 $-x + 1, -y + 2, -z + 1$	#3 $-x + 1, -y + 1, -z$
#4 $x + 1, y, z$	#5 $-x, -y + 1, -z$	#6 $-x, -y, -z$
#7 $-x - 1, -y, -z$	#8 $x, y - 1, z$	#9 $-x + 1, -y + 1, -z + 1$

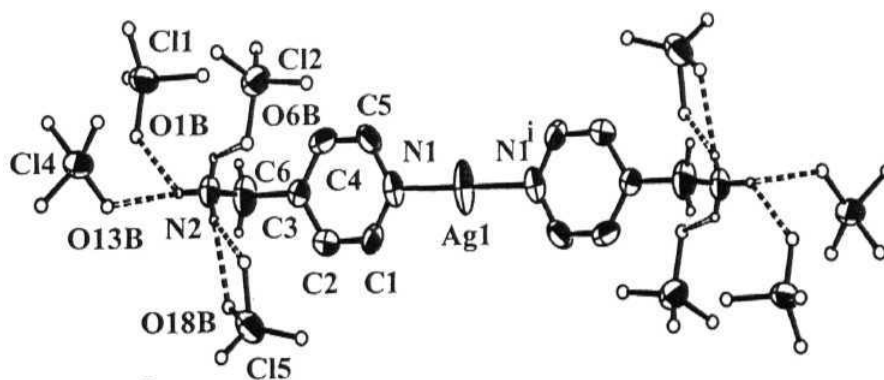
5.2.3. Structure of $\text{Ag}_2(4\text{-pmaH})_4(\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ (2): The asymmetric unit of 2 contains three silver atoms. Ag1 and Ag3 are situated on inversion centers and coordinated to two protonated ligands (Figure 5.3(a) & (c)), whereas Ag2 is coordinated to two crystallographically independent protonated ligands (Figure 5.3(b)), with a linear geometry. Bond lengths and angles are presented in Table 5.5. The geometry around Ag2 is comparable to that of Ag1 in 1, but is more linear than in the previously reported $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$.⁶ There are six anions in the unit cell and all are found to be disordered. In this case, a network of hydrogen bonds are found with 3 different types of geometries, with $\text{H}\cdots\text{A}$ distances in the range 1.63(3) Å to 2.65(8) Å (Table 5.6). Besides, the normal 2-center hydrogen bond and

bifurcated 3-center hydrogen bond, a rarely observed 4-center hydrogen bond is also seen. The 4-center bond is present between HN21 and the acceptors O13Aⁱⁱⁱ, O11Aⁱⁱⁱ and O1Bⁱⁱⁱ. The solvent water molecules 0W1 and 0W2 participates in hydrogen bonding as donors as well as acceptors. It is noteworthy that the hydrogen bond network persists inspite of the positional disorder of the perchlorate O atoms.

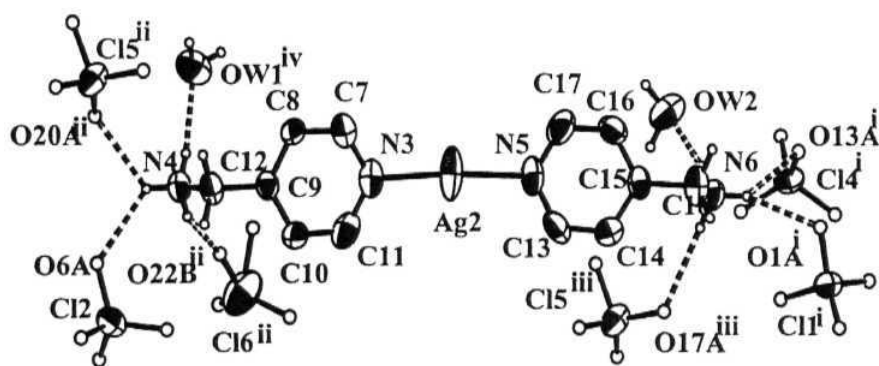
Table 5.5 Bond lengths (Å) and angles (°) for Ag₂(4-pmaH)₄(ClO₄)₆·2H₂O (2).

Ag1-N1#1	2.175(5)	Ag2-N3	2.136(5)	Ag3-N7#2	2.142(5)
Ag1-N1	2.175(5)	Ag2-N5	2.133(5)	Ag3-N7	2.142(5)
N1#1-Ag1-N1	180.0	N5-Ag2-N3	175.0(2)	N7-Ag3-N7#2	180.0

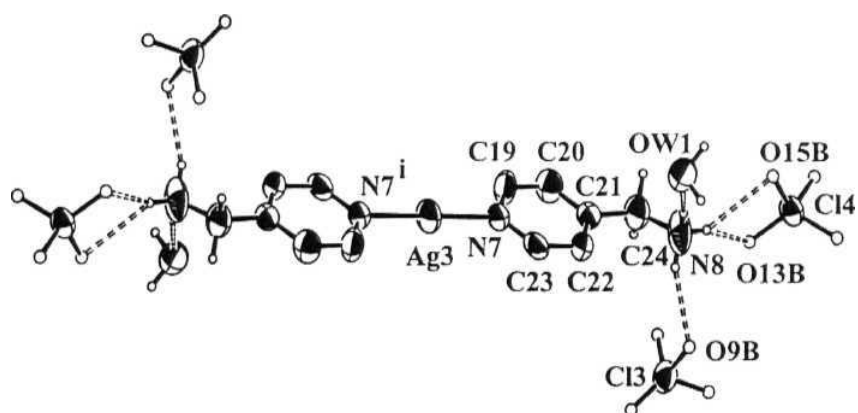
#1 -x, -y + 1, -z + 1 #2 -x + 1, -y + 1, -z



(a)



(b)



(c)

Figure 5.3 Ortep view of the molecular structures of the three different complex cations in **2** with atom labeling. Atoms are represented as 50% probability ellipsoids. Ring hydrogen atoms have been omitted for clarity. Only part of each disordered ClO_4^- ion is shown, with the disordered O atoms represented by circles. Important hydrogen bonds are shown as broken lines. Symmetry codes: in (a): (i) $-x, 1 - y, z$; (ii) $-x, 1 - y, -z$; (iii) $1 - x, -y, -z$; (iv) $-1 + x, y, z$; in (b): (i) $1 - x, -1 + y, z$; (ii) $-x, 1 - y, -z$; (iii) $1 - x, -y, -z$; (iv) $-1 + x, y, z$; in (c): (i) $-x + 1, -y + 1, -z$.

Table 5.6 Hydrogen bonding in $\text{Ag}_2(4\text{-pmaH})_4(\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$ (2).

D-H...A	d(Å)	D(A)	θ (°)	D-H...A	d(A)	D(A)	θ (°)
N2-HN21...O1B#3	2.24	2.89(2)	132	N6-HN62...OW2	1.95	2.814(8)	170
N2-HN21...O13A#3	2.32	3.002(10)	135	N6-HN63...O17A#7	2.19	3.058(13)	175
N2-HN21...O13B#3	2.38	2.93(2)	122	N6-HN63...O17B#7	2.26	3.118(16)	171
N2-HN21...O11A#4	2.62	3.328(14)	140	N8-HN81...O13B#8	2.16	2.97(2)	154
N2-HN22...O5A	2.19	3.058(11)	171	N8-HN81...O15B#8	2.25	3.00(2)	144
N2-HN22...O6B	2.32	2.93(2)	128	N8-HN81...O13A#8	2.28	3.081(11)	153
N2-HN23...O18B#5	2.10	2.92(2)	157	N8-HN81...O15A#8	2.46	3.219(14)	146
N2-HN23...O20B#5	2.35	3.16(2)	154	N8-HN82...O9B#2	1.96	2.758(18)	151
N2-HN23...O18A#5	2.53	3.33(2)	153	N8-HN82...O9A#2	2.50	3.225(12)	142
N4-HN41...O6A	2.20	2.842(11)	130	N8-HN83...OW1	2.00	2.866(9)	171
N4-HN41...O20A#5	2.23	2.844(13)	128	OW1-HW11...O23A#9	2.07(7)	2.796(17)	134(8)
N4-HN41...O20B#5	2.29	2.981(17)	137	OW1-HW11...O23B#9	2.35(6)	3.22(2)	156(8)
N4-HN41...O6B	2.34	2.973(18)	130	OW1-HW11...O21A#9	2.50(8)	3.105(18)	123(7)
N4-HN42...O22B#5	1.86	2.68(2)	155	OW1-HW12...O14A#9	2.03(7)	2.830(12)	141(7)
N4-HN42...O22A#5	2.11	2.978(14)	177	OW1-HW12...O14B#9	2.10(8)	2.87(2)	138(7)
N4-HN43...OW1#3	2.02	2.865(8)	163	OW2-HW21...O15A#2	2.58(10)	3.031(12)	111(7)
N6-HN61...O1B#6	2.10	2.91(2)	155	OW2-HW22...O24B#2	2.14(6)	2.942(19)	151(8)
N6-HN61...O1A#6	2.37	3.091(10)	140	OW2-HW22...O24A#2	2.20(7)	3.026(19)	155(8)
N6-HN61...O13A#6	2.48	3.057(13)	124	OW2-HW22...O21A#2	2.42(6)	3.178(17)	144(7)
N6-HN61...O2A#6	2.52	2.954(10)	112				
#2 $-x+1, -y+1, -z$		#3 $x-1, y, z$		#4 $x-1, y+\frac{1}{2}, z$		#5 $-x, -y+\frac{1}{2}, z$	
#6 $x+1, y-1, z$		#7 $-x+1, -y, -z$		#8 $-x+1, -y+2, -z$		#9 $x+1, y, z$	

5.3. Conclusions

The formation of AgHL^{2+} ($\text{L} = 2\text{-amp}$) was proposed based on solution studies.⁵ Their formation from mineral acid solutions is consistent with the greater affinity of the primary amino group for H^+ , and the affinity of pyridine group for Ag^+ . However, the formation of this type of protonated complexes is rather delicate. The affinity of primary amino group for H^+ may lead to the formation of inorganic salts like NH_4ClO_4 , as observed in case of 3. Thus it is to be understood that the crystallization conditions are very crucial factors which control the formation of complexes with such protonated ligand systems.

In both the structures, the number of potential hydrogen bond acceptor atoms is higher than the number of 'acidic' hydrogen atoms. This is also the case with $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$.⁶ This leads to numerous 3-center (bifurcated - donor type) hydrogen bonds. However, the number of available acceptor atoms is limited by crystal packing constraints. In 1, 13 out of 20 ClO_4^- oxygen atoms and in 2, 9 out of 24 ClO_4^- oxygen atoms and two water oxygen atoms, are able to act as acceptors, while in $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$ only 6 out of 9 oxygen atoms are acting as acceptors. So, if the ratio of available to potential acceptor atoms is considered, in 1, (13/20) and in $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$, (6/9) it is more than 50%, while in 2, (9/24), it is less than 50%. Hence, it appears that to make best use of the hydrogen bonding interactions, the ClO_4^- oxygen atoms in 2 are disordered, which is not the case with 1 or $\text{Ag}(2\text{-pmaH})_2(\text{NO}_3)_3$. Thus, in contrast with the usual situation, where hydrogen bonding inhibits positional disorder, all the ClO_4^- ions in 2 are disordered. We propose that this unusual situation is a consequence of the small number of available acceptors in 2.

5.4. References

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