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Supporting Information

Ancillary Ligands and Spectator Cations as Controlling Factors in the Construction of Coordination and Hydrogen-bonded Networks with the *tert*-Bu-C°CÉAg_n (*n* = 4, 5) Supramolecular Synthon

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Crystal data: **1**, $AgC{\equiv}C^tBu \cdot 3AgCF_3CO_2 \cdot H_2O$, $C_{12}H_{11}F_9O_7Ag_4$, M = 869.67, triclinic, space group $P\bar{1}$ (No. 2), a = 9.150(1) Å, b = 10.815(1) Å, c = 12.026(1) Å, α = 81.705(2) °, β = 76.977(2) °, γ = 68.048(2) °, V = 1073.1(2) Å^3, Z = 2, 3760 unique reflections (R_{int} = 0.0221), $R1$ = 0.0331, $wR2$ = 0.0876, goodness-of-fit = 1.050 for 3353 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model.

2, $AgC{\equiv}C^tBu \cdot 5AgCF_3CO_2 \cdot 4CH_3CN \cdot H_2O$, $C_{24}H_{23}F_{15}O_{11}N_4Ag_6$, M = 1475.67, monoclinic, space group $P2_1/c$ (No. 14), a = 15.600(1), b = 11.119(1), c = 25.696(2) Å, β = 106.189(1) °, V = 4280.5(5) Å^3, Z = 4, 7544 unique reflections (R_{int} = 0.0285), $R1$ = 0.0349, $wR2$ = 0.0896, goodness-of-fit = 1.035 for 5618 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model.

3, $AgC{\equiv}C^tBu \cdot 3AgCF_3CO_2 \cdot CH_3CH_2CN \cdot 2H_2O$, $C_{15}H_{18}F_9O_8NAg_4$, M = 942.75, triclinic, space group $P\bar{1}$ (No. 2), a = 9.957(3) Å, b = 11.438(3) Å, c = 13.168(4) Å, α = 111.976(3) °, β = 105.137(3) °, γ = 101.157(3) °, V = 1269.4(6) Å^3, Z = 2, 4390 unique reflections (R_{int} = 0.0260), $R1$ = 0.0393, $wR2$ = 0.1088, goodness-of-fit = 1.026 for 3052 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model.

4, $AgC{\equiv}C^tBu \cdot 4AgCF_3CO_2 \cdot (CH_3)_3CCN \cdot 2H_2O$, $C_{19}H_{22}F_{12}O_{10}NAg_5$, M = 1191.69, triclinic, space group $P\bar{1}$ (No. 2), a = 9.924(1) Å, b = 11.526(1) Å, c = 15.604(2) Å, α = 109.782(2) °, β = 95.015(2) °, γ = 90.565(2) °, V = 1671.6(3) Å^3, Z = 2, 5777 unique

reflections (R_{int} = 0.0196), $R1$ = 0.0324, $wR2$ = 0.0983, goodness-of-fit = 1.106 for 5043 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model. The fluorine atoms of trifluoroacetate group O1-O2 are differentiated as two parts in 0.60:0.40 ratio.

5, $AgC{\equiv}C^tBu \cdot 4AgCF_3CO_2 \cdot (BnMe_3N)(CF_3CO_2) \cdot 2H_2O$, $C_{26}H_{29}F_{15}O_{12}NAg_5$, M = 1371.82, triclinic, space group $P\bar{1}$ (No. 2), a = 10.449(2) Å, b = 14.109(2) Å, c = 14.447(2) Å, α = 88.877(3) °, β = 82.121(3) °, γ = 81.972(3) °, V = 2089.0(5) Å^3, Z = 2, 10178 unique reflections (R_{int} = 0.0274), $R1$ = 0.0430, $wR2$ = 0.1180, goodness-of-fit = 1.013 for 6347 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model. All fluorine atoms of five independent trifluoroacetate groups are disordered at two positions in the ratio of 0.5:0.5.

6, $AgC{\equiv}C^tBu \cdot 4AgCF_3CO_2 \cdot (Et_4N)(CF_3CO_2) \cdot 2H_2O$, $C_{24}H_{33}F_{15}O_{12}NAg_5$, M = 1351.83, triclinic, space group $P\bar{1}$ (No. 2), a = 10.198(1) Å, b = 14.492(2) Å, c = 15.666(2) Å, α = 107.575(2) °, β = 105.789(2) °, γ = 96.712(2) °, V = 2073.4(4) Å^3, Z = 2, 10082 unique reflections (R_{int} = 0.0325), $R1$ = 0.0487, $wR2$ = 0.1400, goodness-of-fit = 1.023 for 5794 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model. The fluorine atoms of trifluoroacetate groups O5-O6 and O7-O8 were processed into two disordered parts in 0.65:0.35 ratio. Partial carbon atoms of tetraethylammonium cations were differentiated as two disordered parts, whose hydrogen atoms were not added.

7, $AgC{\equiv}C^tBu \cdot 4AgCF_3CO_2 \cdot ({}^nPr_4N)(CF_3CO_2) \cdot 2H_2O$, $C_{28}H_{41}F_{15}O_{12}NAg_5$, M = 1407.94, triclinic, space group $P\bar{1}$ (No. 2), a = 10.394(1) Å, b = 14.488(2) Å, c = 15.259(2) Å, α = 97.042(2) °, β = 96.745(2) °, γ = 97.298(2) °, V = 2241.3(4) Å^3, Z = 2, 10914 unique

reflections (R_{int} = 0.0282), $R1$ = 0.0440, $wR2$ = 0.1240, goodness-of-fit = 1.011 for 6545 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model. The *tert*-butyl moiety of ethynide ligand *t*BuC≡C$^-$ and the fluorine atoms of trifluoroacetate groups O5-O6 and O9-O10 were differentiated as two parts in the ratio of 0.55:0.45.

8, AgC≡C^{t}Bu · 4AgCF$_3$CO$_2$ · 3[(^{n}Bu$_4$N)(CF$_3$CO$_2$)] · H$_2$O, $C_{68}H_{119}F_{21}O_{15}N_3Ag_5$, M = 2157.00, Orthorhombic, space group *Pnma* (No. 62), a = 26.905(3) Å, b = 25.495(3) Å, c = 13.836(2) Å, V = 9491(2) Å^3, Z = 4, 12089 unique reflections (R_{int} = 0.0840), $R1$ = 0.0594, $wR2$ = 0.2288, goodness-of-fit = 0.989 for 4661 observed reflections with $I > 2\sigma(I)$. The water hydrogen atoms were not included in the structure model. The fluorine atoms of three trifluoroacetate groups (O1-O2, O3-O4 and O7-O8) were processed into two disordered parts in the ratio of 0.55:0.45.