

Table S1. Stability constants obtained when considering other equilibrium than the one for the formation of [Ag(L)] (complex [Ag₂(PIPES)] or [Ag(MES)₂]).

Buffer	pKa	Stability constants
PIPES	6.647(6), 2.54(2), 1.3(4)	$\log(\beta_{1,1}^{\text{Ag,B}}) = 1.5(2)$, $\log(\beta_{2,1}^{\text{Ag,B}}) = 1.5(2)$
MES	6.00(2), 0.1(6)	$\log(\beta_{1,1}^{\text{Ag,B}}) = 1.5(2)$, $\log(\beta_{1,2}^{\text{Ag,B}}) = 3.5(4)$

Table S2. Bond distances (Ag-donor atom), average bond valences ($v_{\text{Ag,N1X2}}$ and $v_{\text{Ag,O3-5}}$)^a and total atom valence (V_{Ag})^b in the molecular structures of [Ag_x(Buffer)_m].

	[Ag(HEPES)] ^[1]	[Ag ₂ (μ-H ₂ O)(PIPES)] ^{[2] c}	[Ag ₂ (MES) ₂ (BisBz)] ^[3]	[Ag(TEOA) ₂] ^[4]
Ag-N _{1,buffer} / Å	2.266(3)	2.309(5)	2.155(2)	2.276(3)
Ag-X _{2, strong} / Å	X = N _{buffer} 2.280(3)	X = O _{sulfonate} 2.33(3)	X = N _{BisBz} 2.285(2)	X = N _{buffer} 2.346(4)
Ag-O ₃ / Å	2.581(2)	2.49(3)	2.479(2)	2.660(4)
Ag-O ₄ / Å	2.666(2)	2.54(2)	2.516(2)	2.675(4)
Ag-O ₅ / Å	NA	NA	NA	2.717(5)
$v_{\text{Ag,N1X2}}$ ^d	0.319(8)	0.28(2)	0.37(9)	0.29(4)
$v_{\text{Ag,O3-5}}$ ^e	0.13(2)	0.17(2)	0.17(1)	0.105(9)
V_{Ag}	0.888	0.91(5)	1.101	0.894

^a $v_{\text{Ag},j} = e^{[(R_{\text{Ag},j} - \delta_{\text{Ag},j})/b]}$, whereby $\delta_{\text{Ag},j}$ is the Ag-donor atom j distance. The valence bond parameters $R_{\text{Ag},\text{N}}$ and $R_{\text{Ag},\text{O}}$ are taken from ref. [5] and $b = 0.37$ Å. ^b $V_{\text{Ag}} = \sum_j v_{\text{Ag},j}$.^[5] ^c Each value corresponds to the average of the two different environments of silver(I) in the crystal structure. The numbers between brackets are the estimated standard deviations associated with the averaging process. NA = not applicable because the silver is only tetracoordinated. ^d $v_{\text{Ag,N1X2}}$ corresponds to average bond valences for the two strongest coordination bonds i.e. with N₁ and X₂. ^e $v_{\text{Ag,O3-5}}$ corresponds to average bond valences for the weaker coordination bonds i.e. with O₃, O₄ and O₅ for Tris.

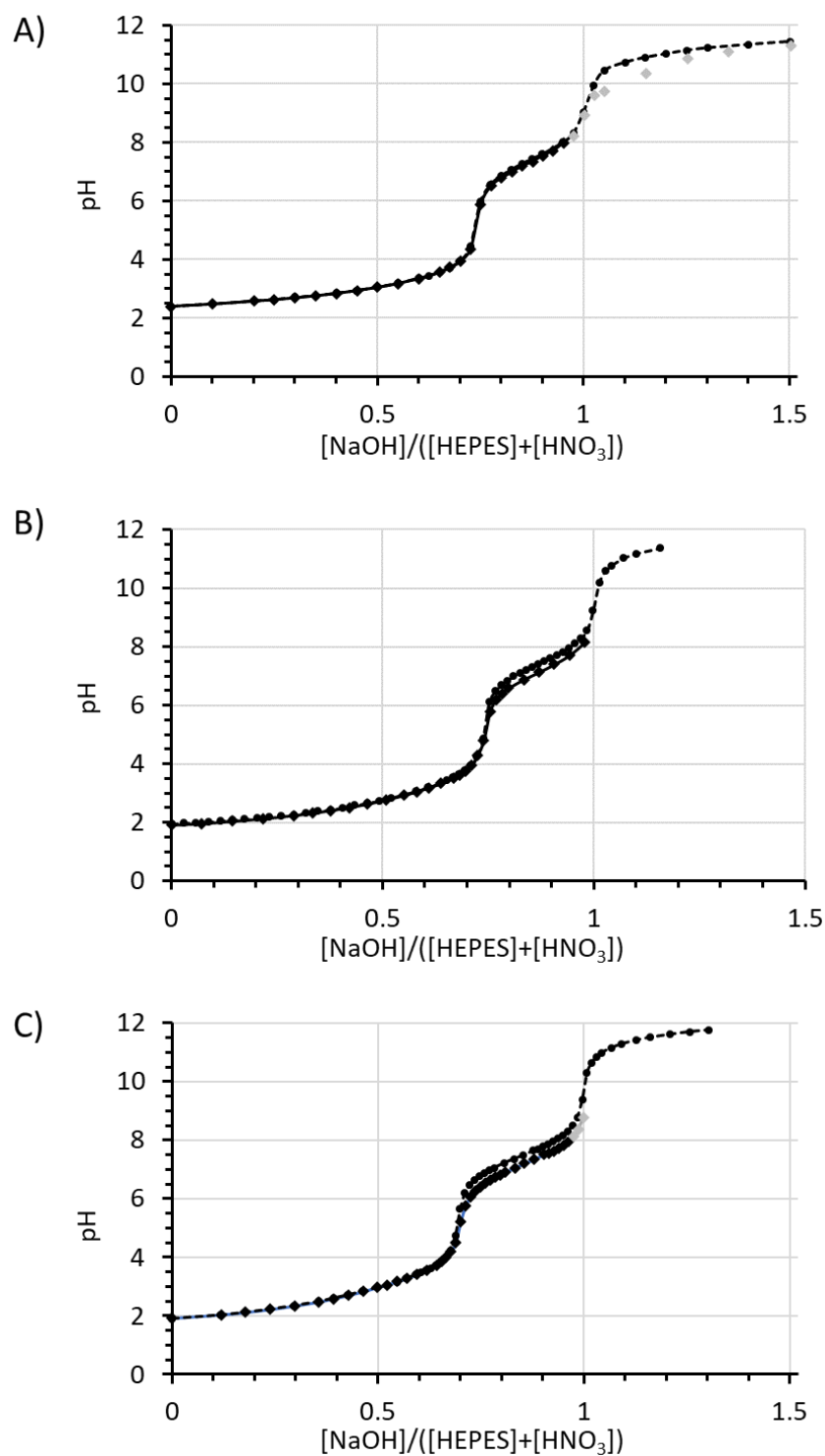


Figure S1. Titration curves obtained for HEPES without (circles, dashed line) and in presence of silver nitrate (diamonds, plain line, grey points are over pH 8.0 and removed from for fitting data) in solution (initial volume 50 mL) with constant ionic strength (NaNO_3 0.1 M). A) HEPES (0.10 mmol), HNO_3 (0.30 mmol), AgNO_3 (0.05 mmol). B) HEPES (0.36 mmol), HNO_3 (1.02 mmol), AgNO_3 (0.25 mmol). C) HEPES (0.51 mmol), HNO_3 (1.17 mmol), AgNO_3 (0.42 mmol).

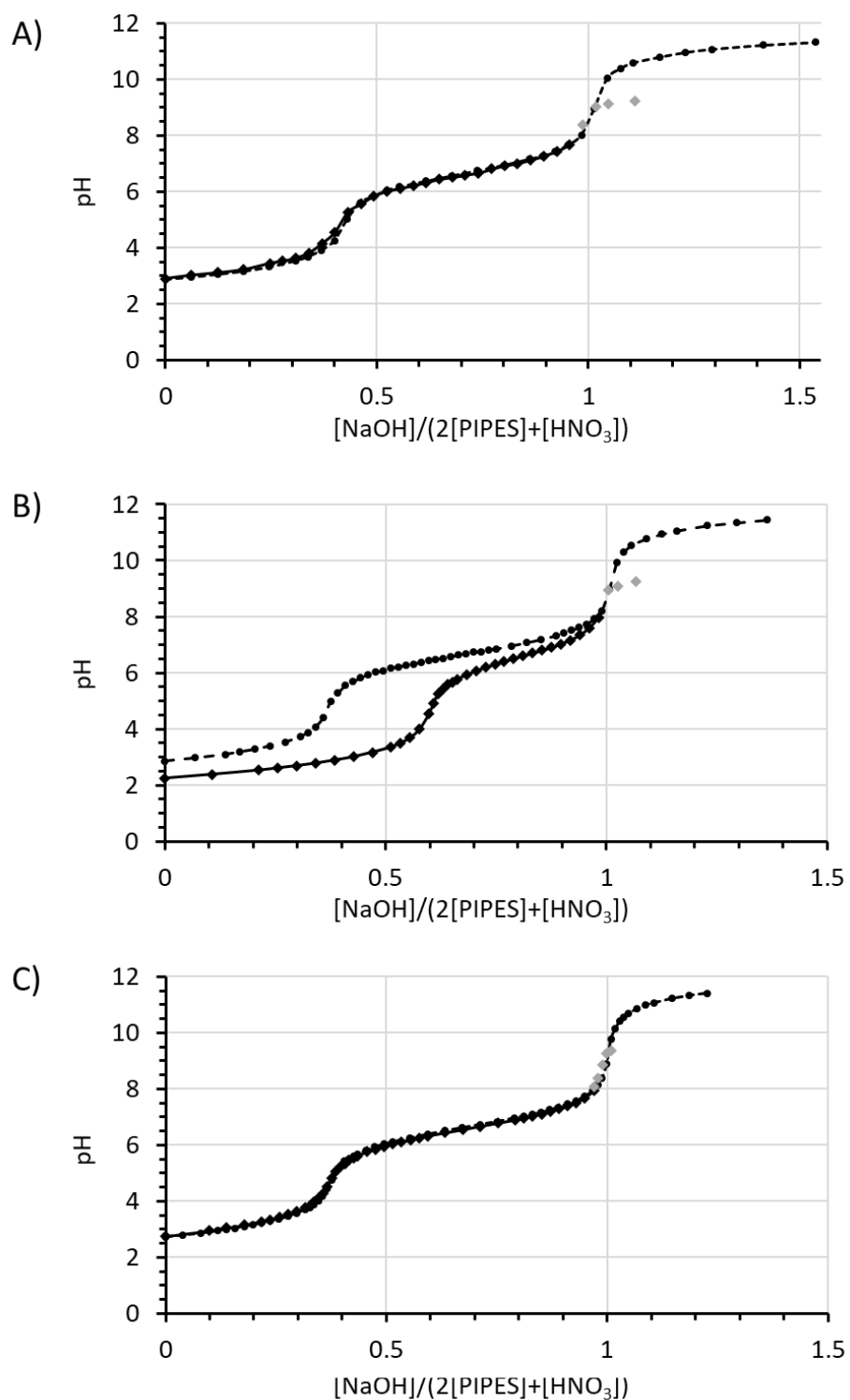


Figure S2. Titration curves obtained for PIPES without (circles, dashed line) and in presence of silver nitrate (diamonds, plain line, grey points are over pH 8.0 and removed from for fitting data) in solution (initial volume 50 mL) with constant ionic strength (NaNO_3 0.1 M). A) PIPES (0.17 mmol), HNO_3 (0.19 mmol), AgNO_3 (0.14 mmol). B) PIPES (0.34 mmol), HNO_3 (0.32 mmol) without silver and 0.64 mmol with silver, AgNO_3 (0.19 mmol). C) PIPES (0.59 mmol), HNO_3 (0.56 mmol), AgNO_3 (0.16 mmol).

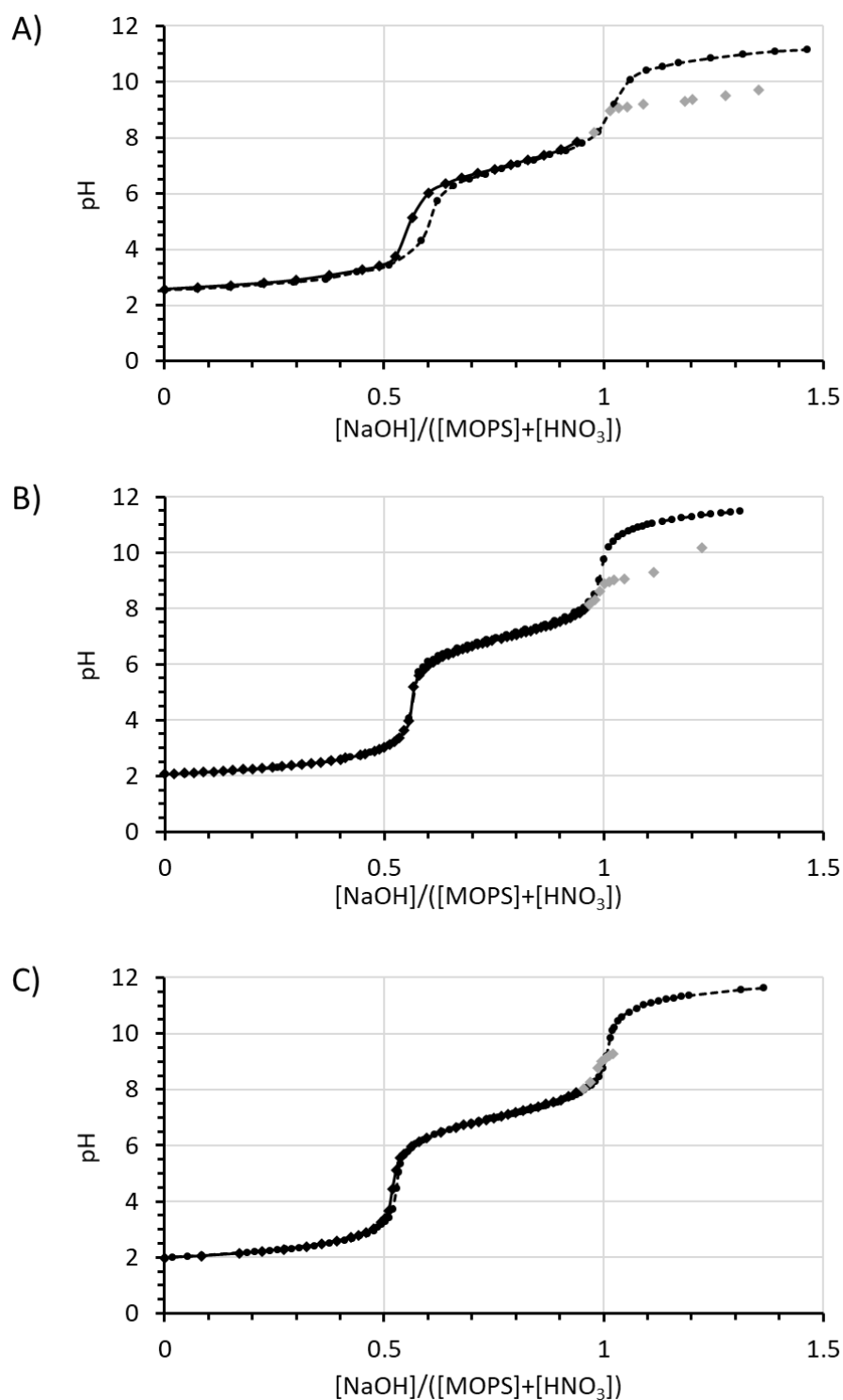


Figure S3. Titration curves obtained for MOPS without (circles, dashed line) and in presence of silver nitrate (diamonds, plain line, grey points are over pH 8.0 and removed from for fitting data) in solution (initial volume 50 mL) with constant ionic strength (NaNO_3 0.1 M). A) MOPS (0.10 mmol), HNO_3 (0.15 mmol without silver and 0.14 mmol with silver), AgNO_3 (0.10 mmol). B) MOPS (0.36 mmol), HNO_3 (0.46 mmol), AgNO_3 (0.18 mmol). C) MOPS (0.51 mmol), HNO_3 (0.56 mmol), AgNO_3 (0.14 mmol).

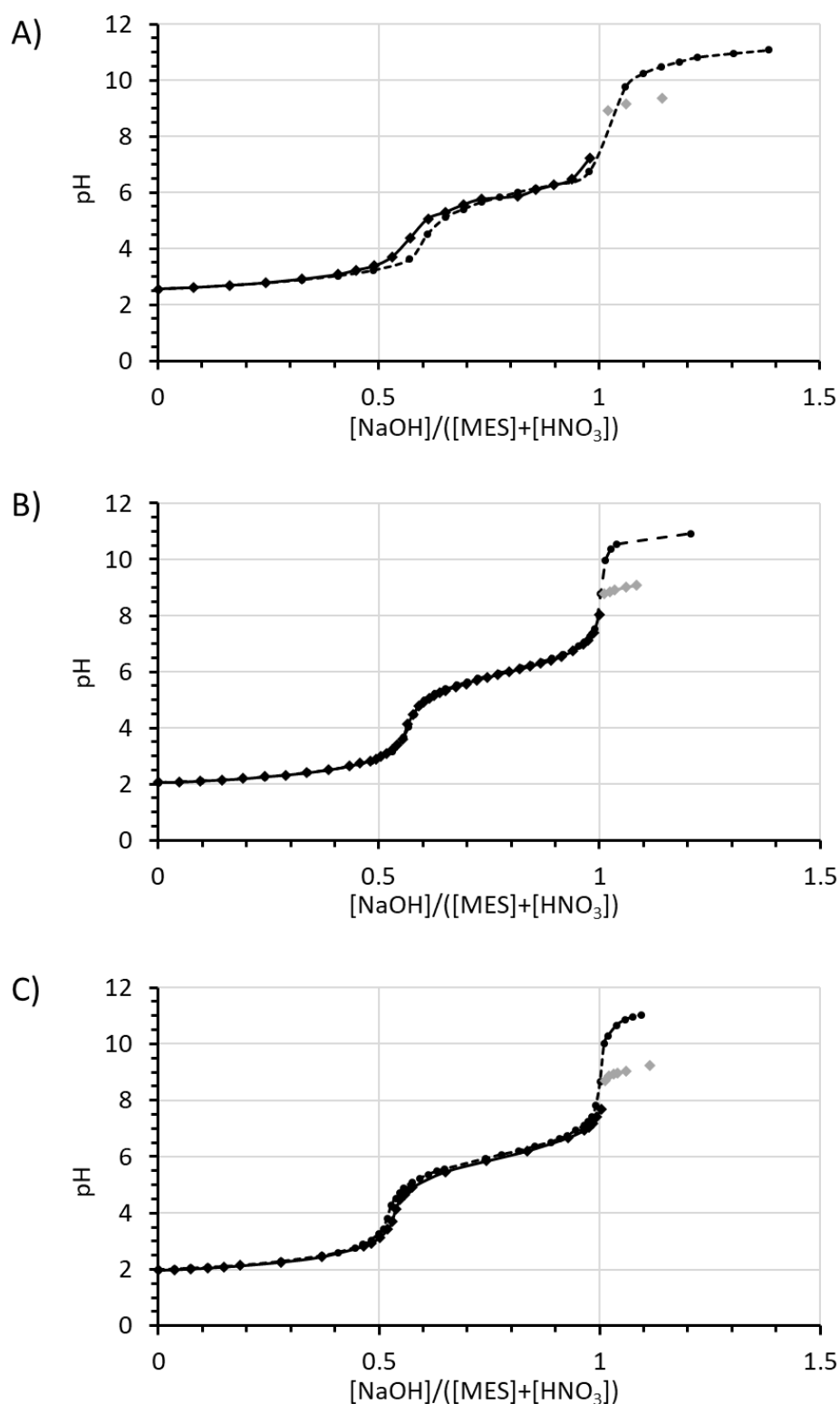


Figure S4. Titration curves obtained for MES without (circles, dashed line) and in presence of silver nitrate (diamonds, plain line, grey points are over pH 8.0 and removed from for fitting data) in solution (initial volume 50 mL) with constant ionic strength (NaNO_3 0.1 M). A) MES (0.10 mmol), HNO_3 (0.14 mmol), AgNO_3 (0.08 mmol). B) MES (0.35 mmol), HNO_3 (0.47 mmol), AgNO_3 (0.18 mmol). C) MES (0.50 mmol), HNO_3 (0.56 mmol), AgNO_3 (0.21 mmol).

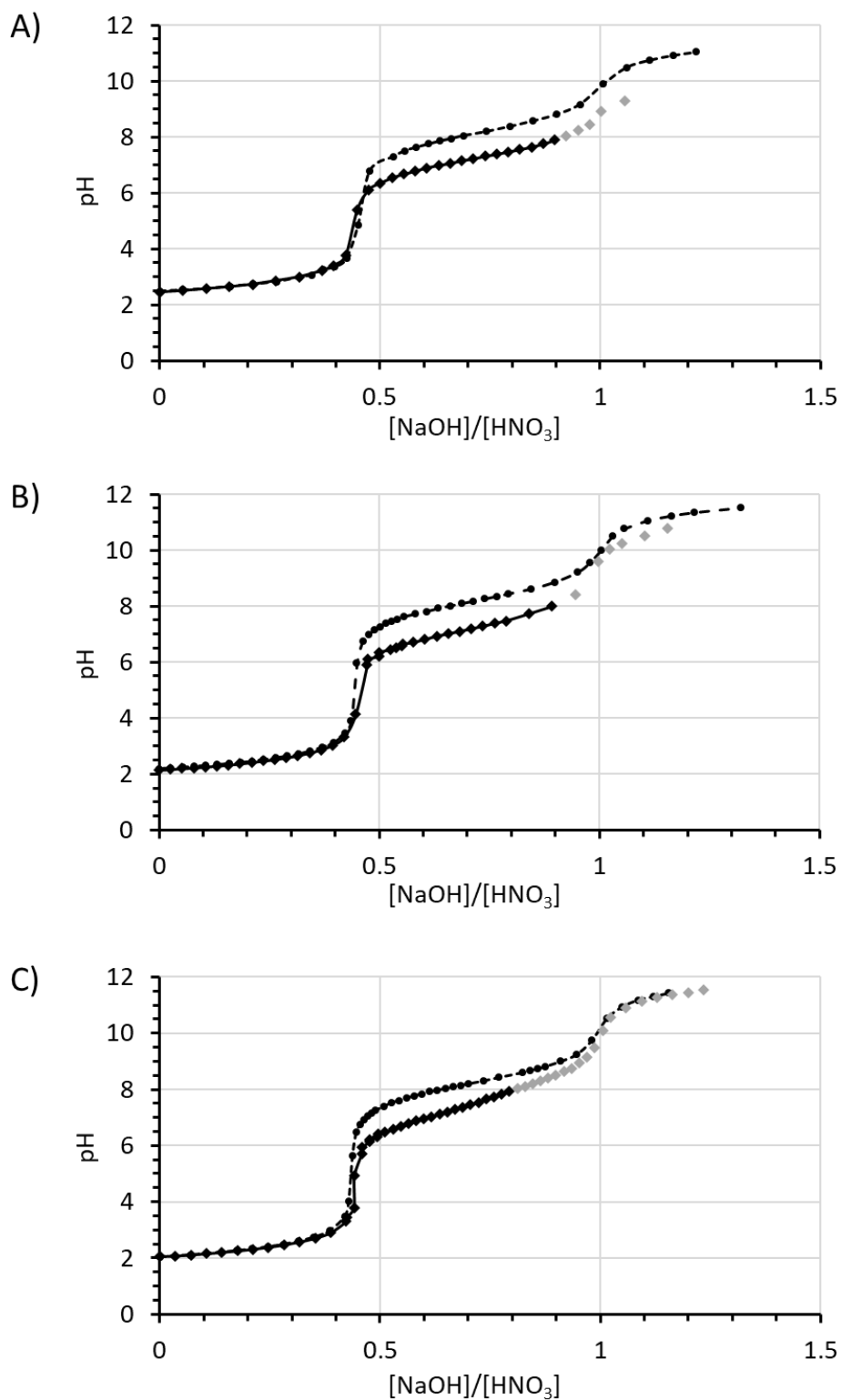


Figure S5. Titration curves obtained for Tris without (circles, dashed line) and in presence of silver nitrate (diamonds, plain line, grey points are over pH 8.0 and removed from for fitting data) in solution (initial volume 50 mL) with constant ionic strength (NaNO_3 0.1 M). A) Tris (0.20 mmol), HNO_3 (0.37 mmol), AgNO_3 (0.21 mmol). B) Tris (0.40 mmol), HNO_3 (0.75 mmol), AgNO_3 (0.21 mmol). C) Tris (0.60 mmol), HNO_3 (1.12 mmol), AgNO_3 (0.16 mmol).

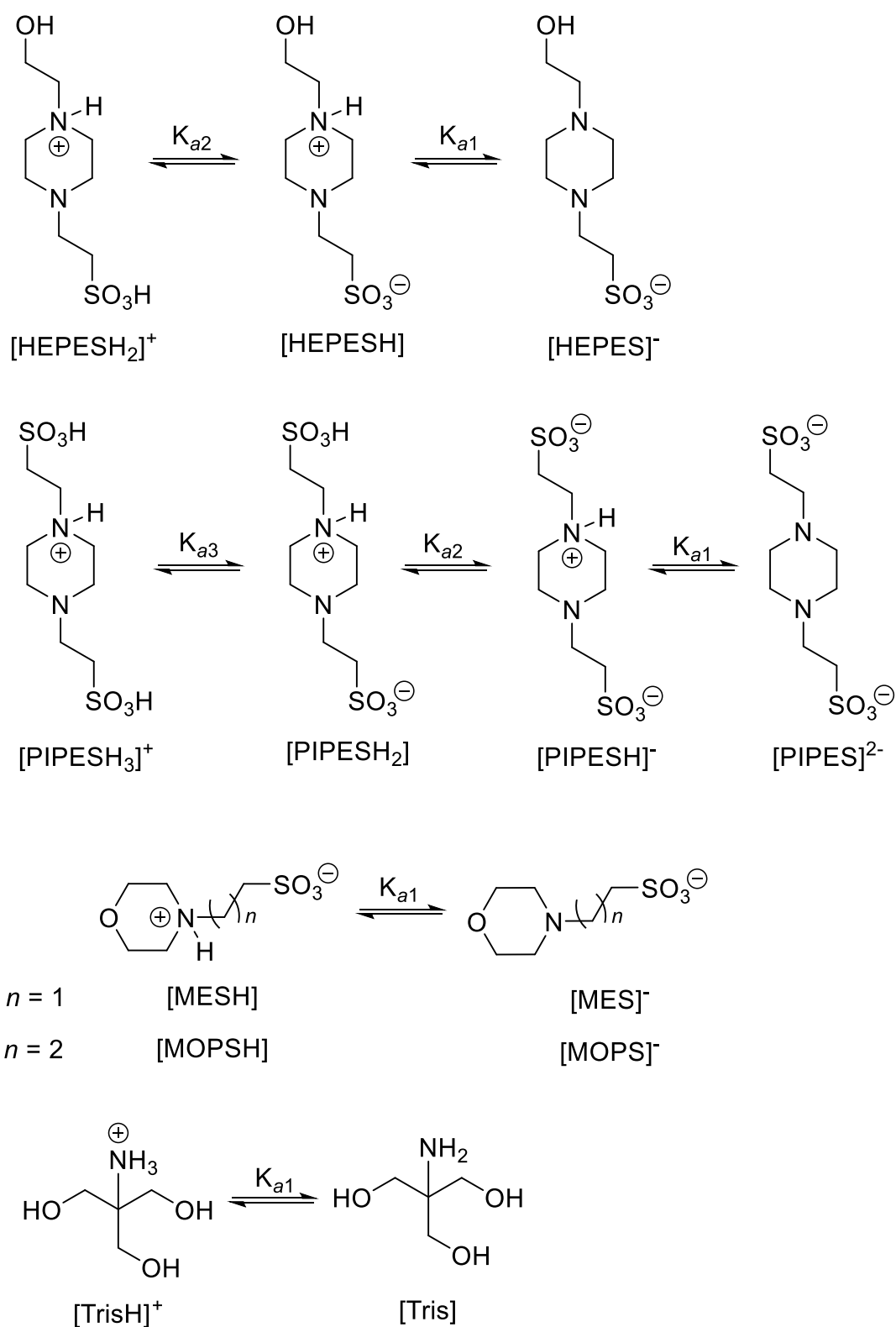


Figure S6. Acid dissociation equilibria considered in the present study for the different buffers.

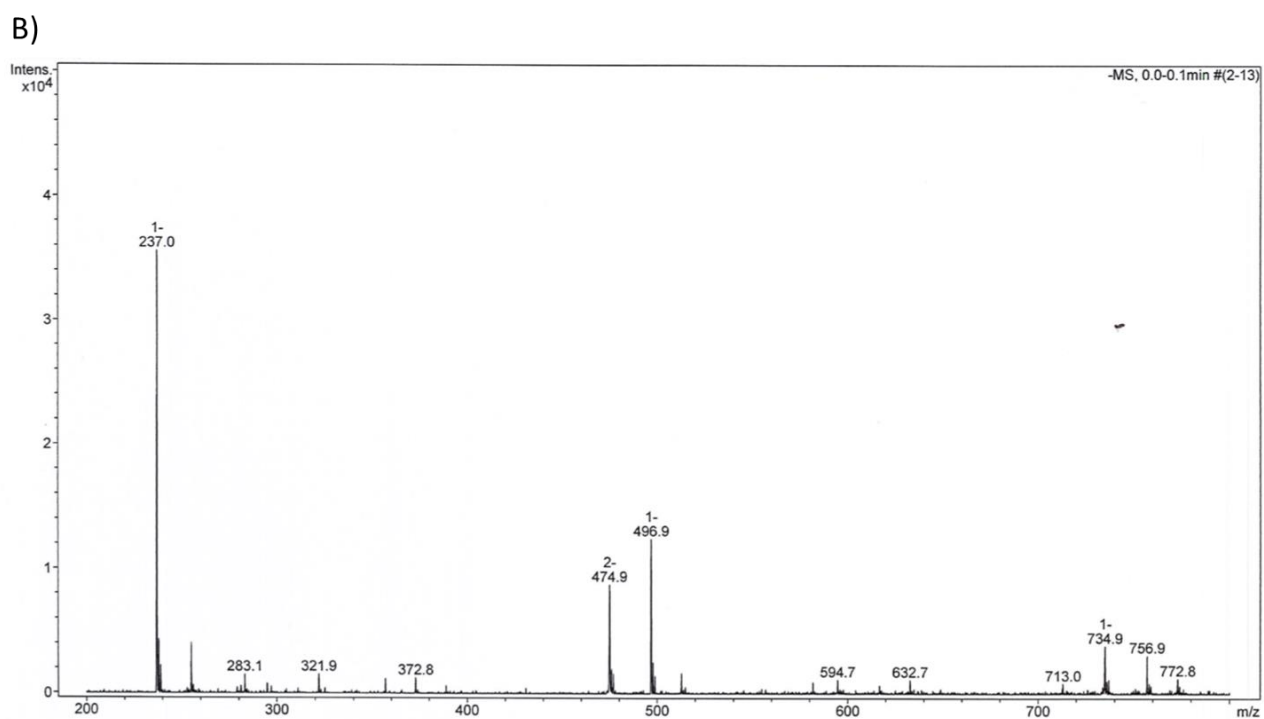
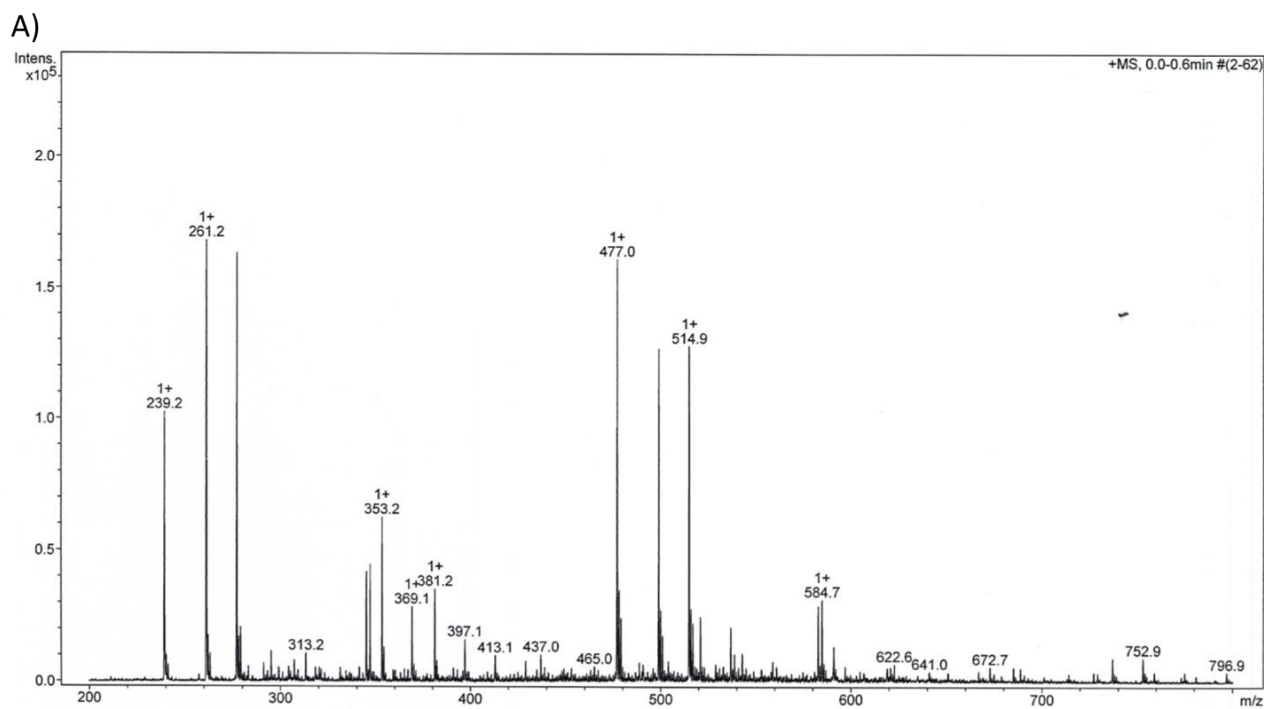
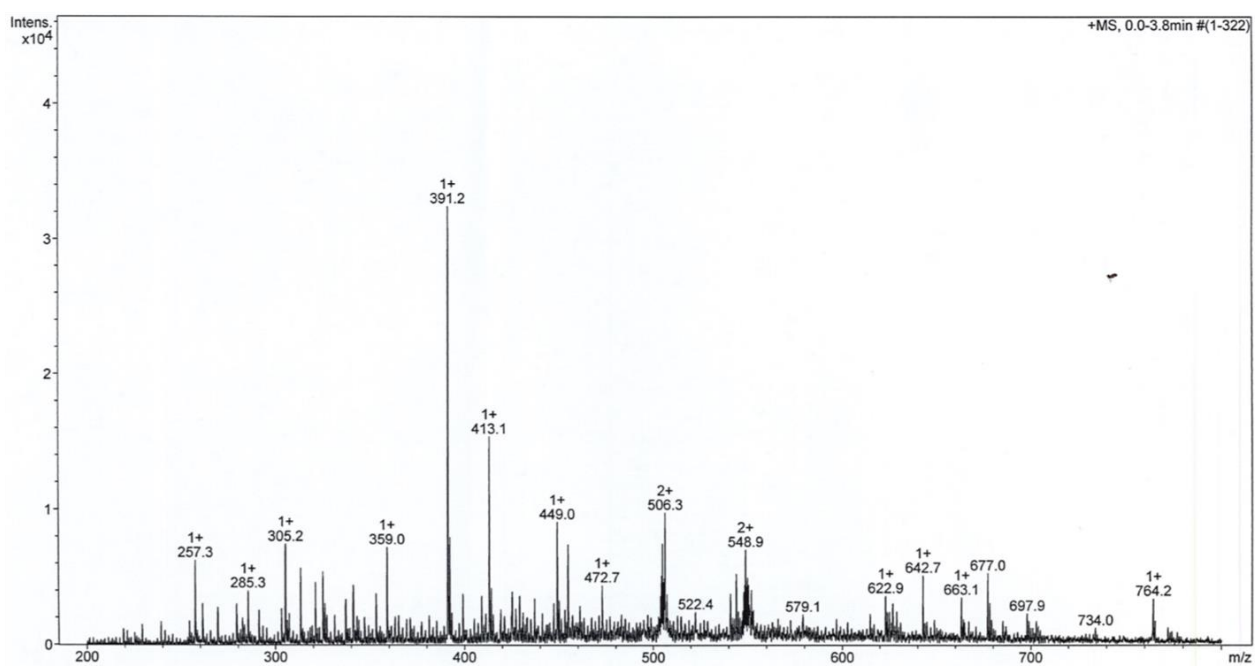


Figure S7. Mass spectra in A) positive and B) negative mode for HEPES buffer with silver nitrate.

A)



B)

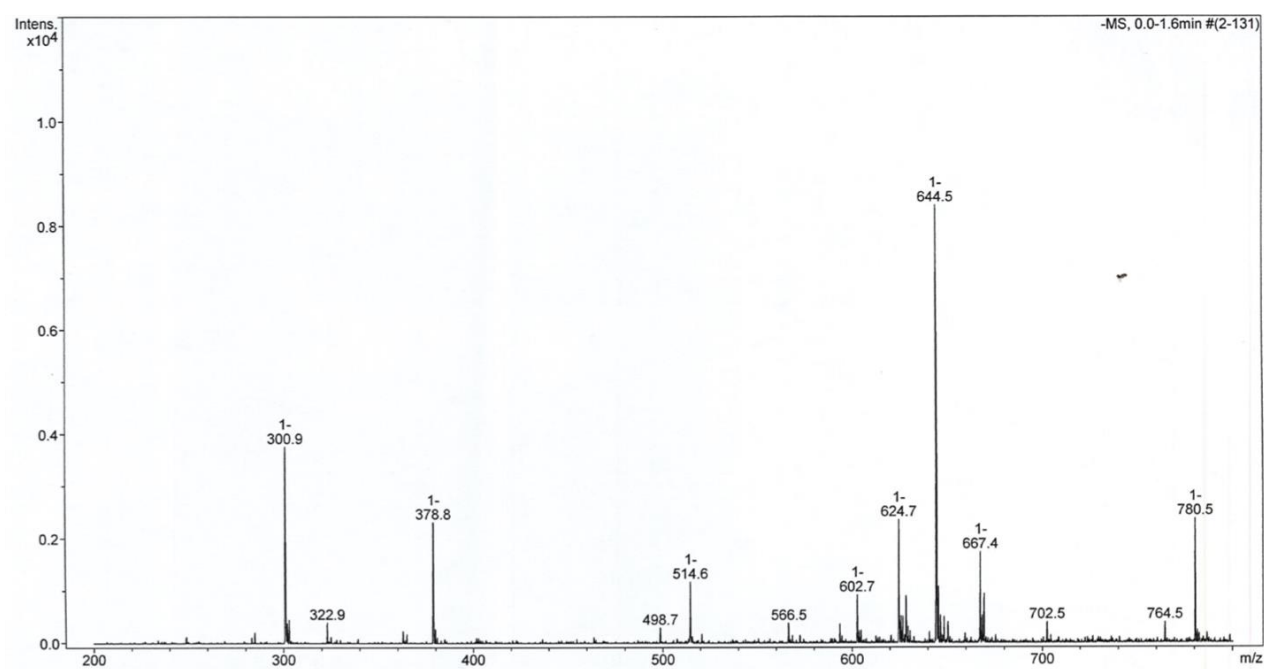
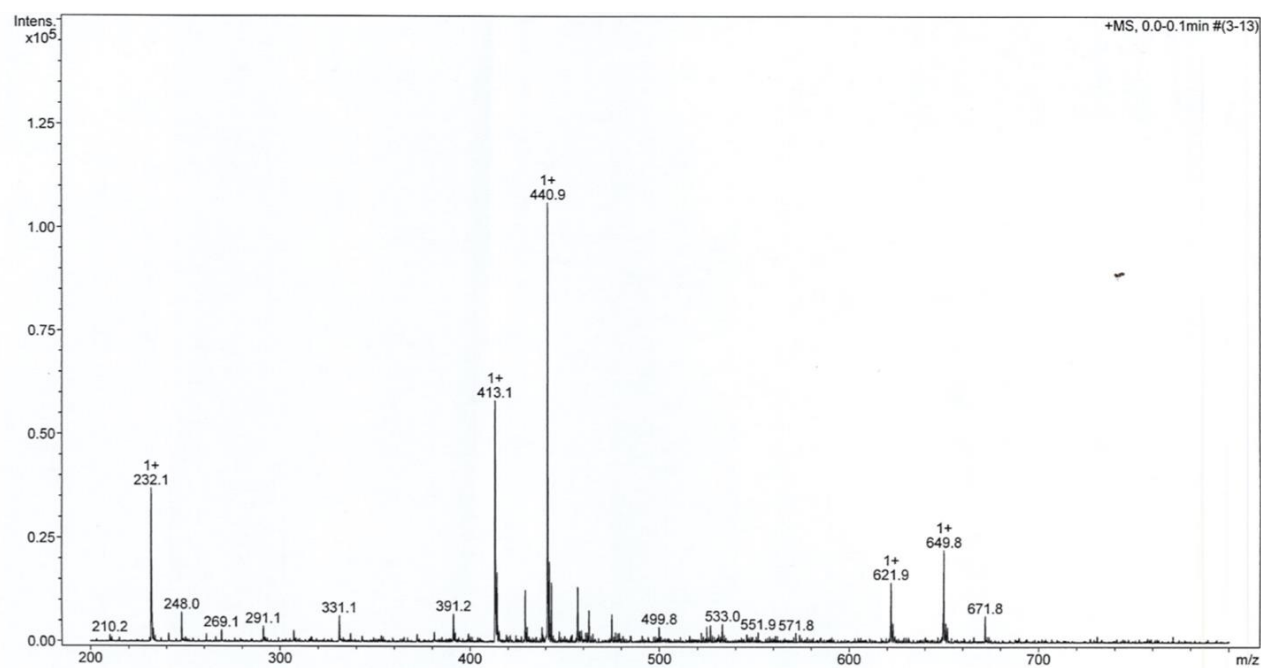


Figure S8. Mass spectra in A) positive and B) negative mode for PIPES buffer with silver nitrate.

A)



B)

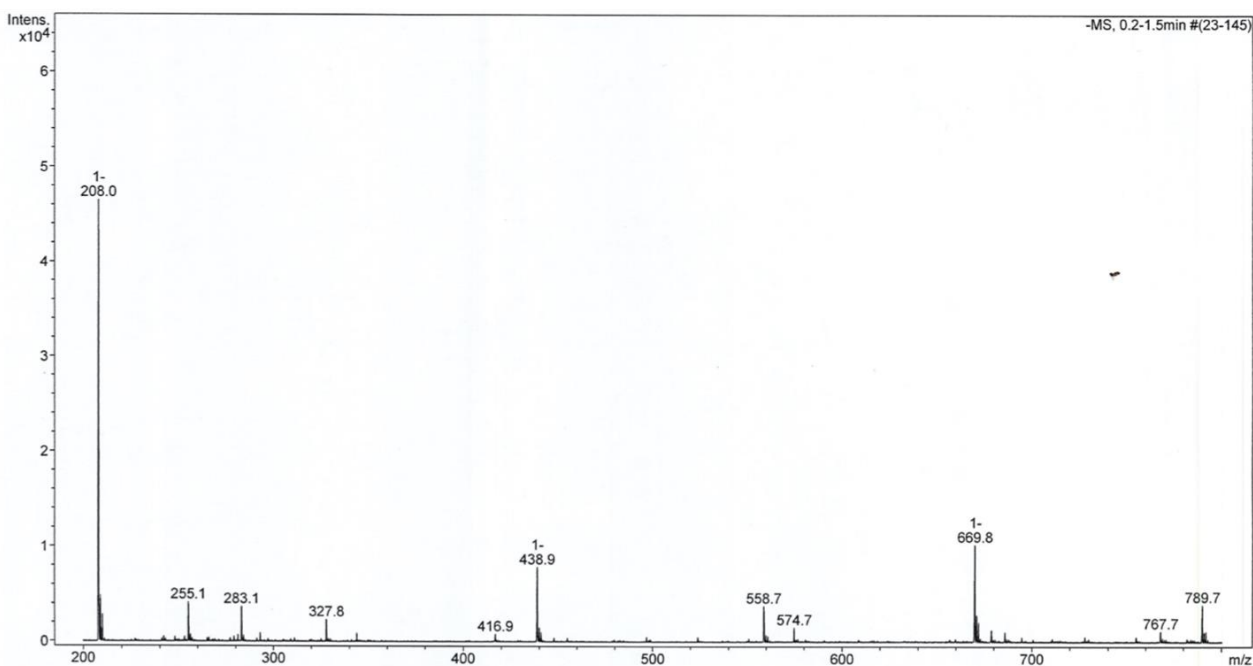


Figure S9. Mass spectra in A) positive and B) negative mode for MOPS buffer with silver nitrate.

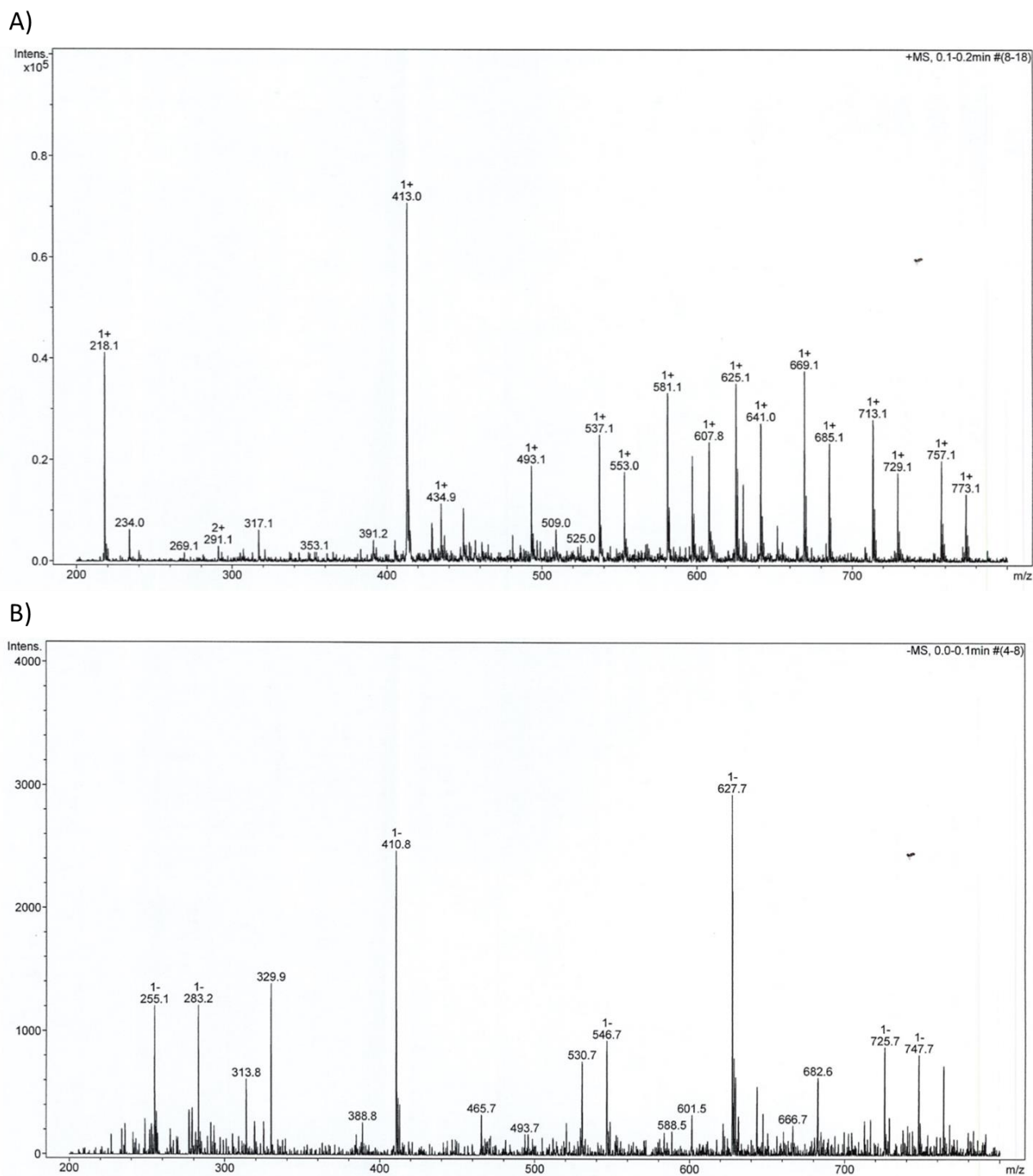


Figure S10. Mass spectra in A) positive and B) negative mode for MES buffer with silver nitrate.

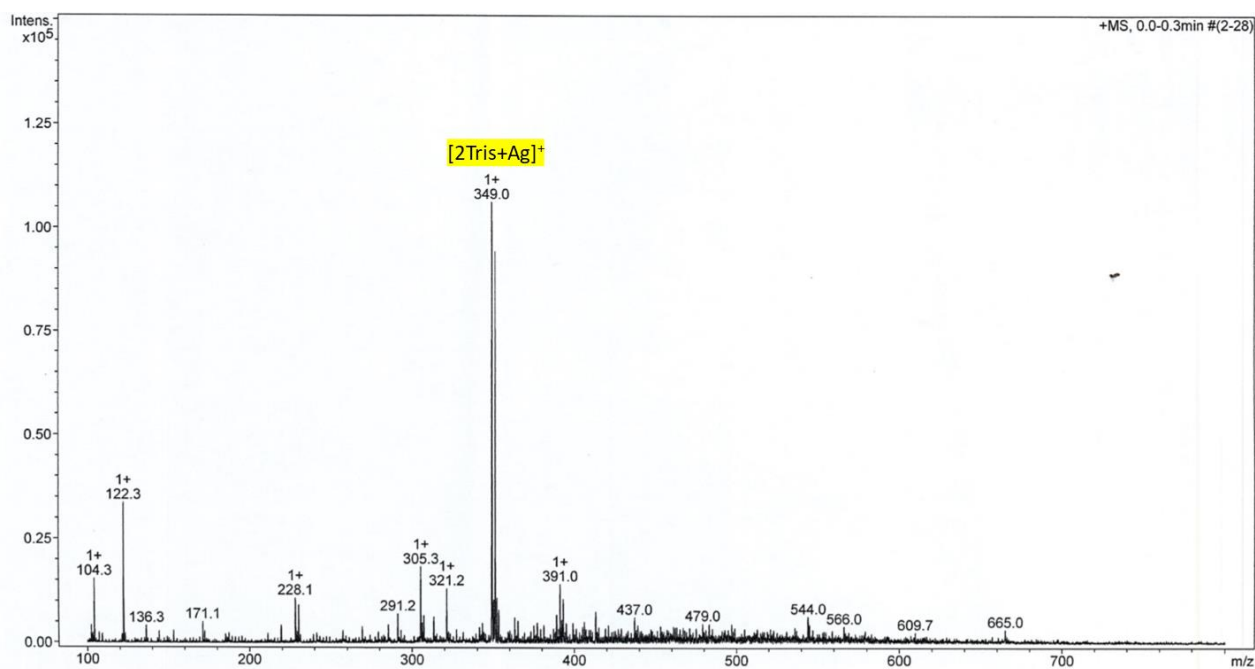


Figure S11. Mass spectra in positive mode for Tris buffer with silver nitrate.

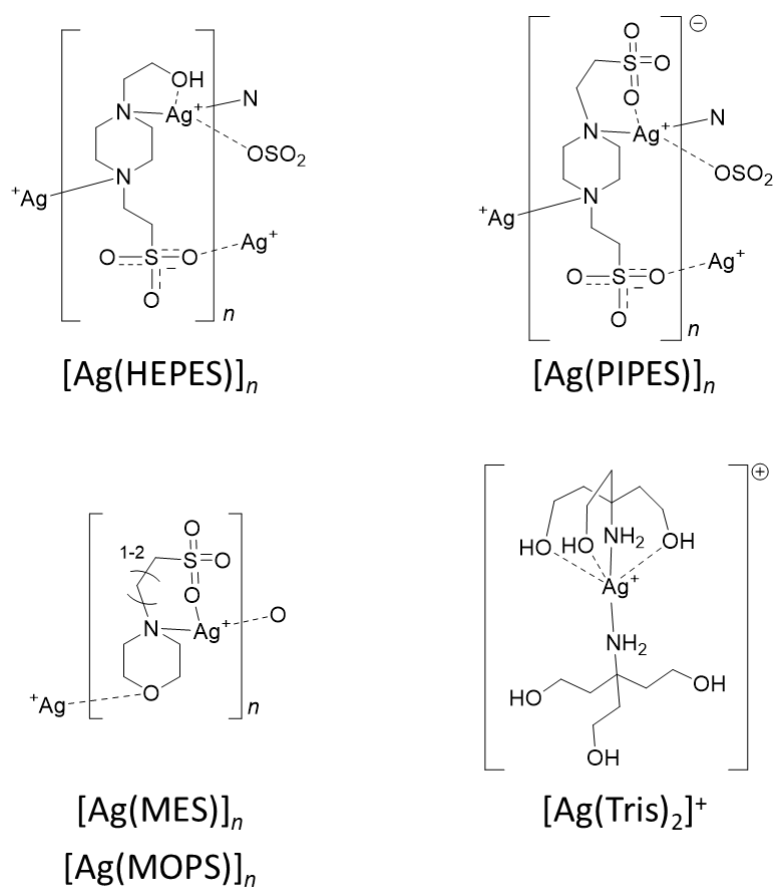


Figure S12. Proposed structures of complexes formed with silver. This stoichiometry was retained for determination of stability constants.

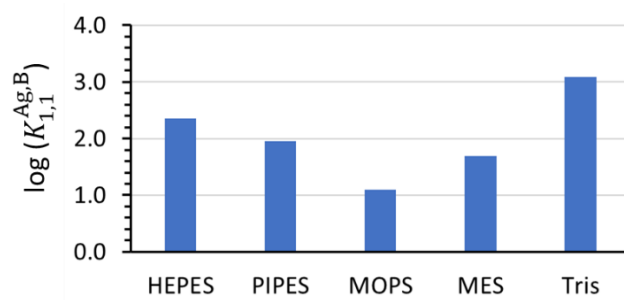


Figure S13. Logarithm of stability constants $K_{1,1}^{Ag,B}$ for the first complexation of silver(I) on ligands B (B= buffer studied in this paper).

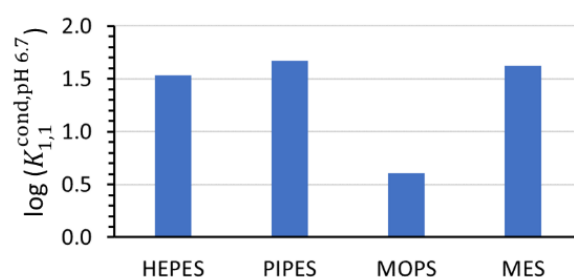


Figure S14. Logarithm of conditional (or apparent) stability constants $K_{1,1}^{cond,pH 6.7}$ for the first complexation of silver(I) on buffers at a fixed pH value $pH = 6.7$.

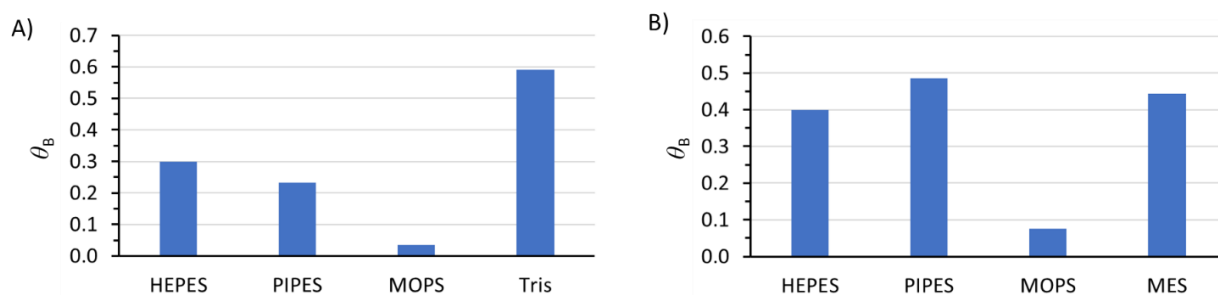


Figure S15. Fraction of silver bound to the buffer. A) Total concentration of buffer 4 mM and silver 40 μ M at pH 7.4. B) Total concentration of buffer 20 mM and silver 1 mM at pH 6.7.

References

- [1] S. M. Bilinovich, M. J. Panzner, W. J. Youngs, T. C. Leeper, *Acta Crystallogr. E* **2011**, 67, 1178-1179.
- [2] S. Daofeng, C. Rong, L. Yucang, H. Maochun, *Chem. Lett.* **2002**, 31, 198-199.
- [3] H. Jiang, J.-F. Ma, W.-L. Zhang, Y.-Y. Liu, J. Yang, G.-J. Ping, Z.-M. Su, *Eur. J. Inorg. Chem.* **2008**, 2008, 745-755.
- [4] R. Kumar, S. Obrai, A. Kaur, M. S. Hundal, H. Meehnian, A. K. Jana, *New J. Chem.* **2014**, 38, 1186-1198.
- [5] a) N. E. Brese, M. O'Keeffe, *Acta Crystallogr. B* **1991**, 47, 192-197; b) O. C. Gagne, F. C. Hawthorne, *Acta Crystallogr. B* **2015**, 71, 562-578.