Electronic Supplementary Information

Specific and Non-Specific Interactions between Metal Cation and Zwitterionic Alanine Tripeptide in Saline Solutions Reported by the Symmetric Carboxylate Stretching and Amide-II Vibrations

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1. Frequency difference of the COO- stretching modes

Table S1. Peak positions of the I_{ss} and I_{as} (in cm^{-1}) determined from derivative of the FTIR spectra of Ala3 in D_2O and in the four saline solutions each at 5 M concentration. $\Delta\nu_{a\text{-}s}$ of each case is shown for comparison.

	ν (I_{as})	ν (I_{ss})	$\Delta\nu_{a\text{-}s}$
D_2O	1590.9	1408.3	182.6
NaCl	1589.3	1409.2	180.1
$CaCl_2$	1583.2/1610 [a]	1412.8	170.4/197.2
$MgCl_2$	1582.5/1596 [b]	1414.3	168.2/181.7
$ZnCl_2$	1588.9/1632 [c]	1411.6	177.3/220.4

a. Two peaks appear in the I_{as} component at 5 M $CaCl_2$ concentrations, but the blue-shifted (high-frequency) component overlaps with the I_2 mode, thus their peak positions are not well resolved.

b. Two peaks appear in the I_2 component at higher $MgCl_2$ concentrations according to difference spectra, but the red-shifted (low-frequency) component overlaps with the I_{as} component while the blue-shifted (high-frequency) component overlaps with the I_1 mode, thus their peak positions are not well resolved.

c. Two peaks appear in the I_{as} component at higher $ZnCl_2$ concentrations, but the blue-shifted (high-frequency) component overlaps with the I_2 mode, thus their peak positions are not well resolved.

2. Additional MD simulations and data analysis using the Amber94 force field.[1]

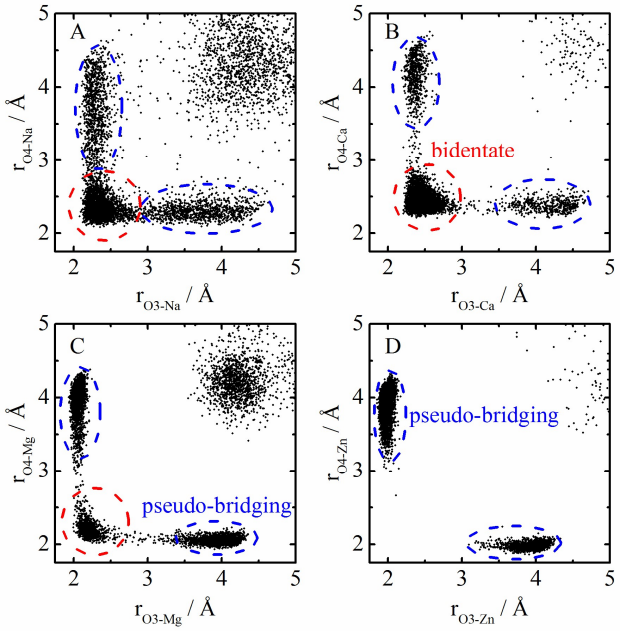
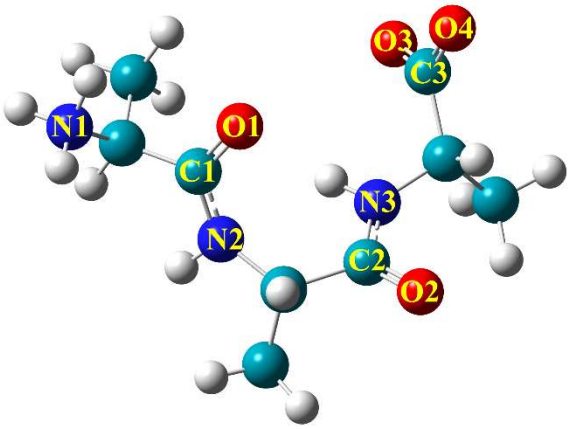


Fig. S1. Joint distribution of two nearest cation-oxygen distances for the zwitterionic Ala3 in four saline solutions. Dashed circles indicate the population of the bidentate form, whereas dashed oval indicate that of the pseudo-bridging form. Scattered distributions on the upper right corner in each case may indicate the binding of metal cation to the COO^- group via a water molecule. Oxygen atoms are labeled in Scheme S1.



Scheme S1. Zwitterionic alanine tripeptide (Ala3) in an arbitrary conformation. Atoms and labelings: N1 belongs to the ND_3^+ group; C1O1N2D is amide unit 1; C2O2N3D is amide unit 2; C3O3O4 is the COO^- group.

3. References

(1) Cornell, W. D.; Cieplak, P.; Bayly, C. I.; Gould, I. R.; Merz, K. M.; Ferguson, D. M.; Spellmeyer, D. C.; Fox, T.; Caldwell, J. W.; Kollman, P. A. A Second Generation Force Field for the Simulation of Proteins, Nucleic Acids, and Organic Molecules. *J. Am. Chem. Soc.* **1995**, *117*, 5179-5197.