Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

The Interaction of NOTA as a Bifunctional Chelator with Competitive Alkali Metal ions: A DFT Study

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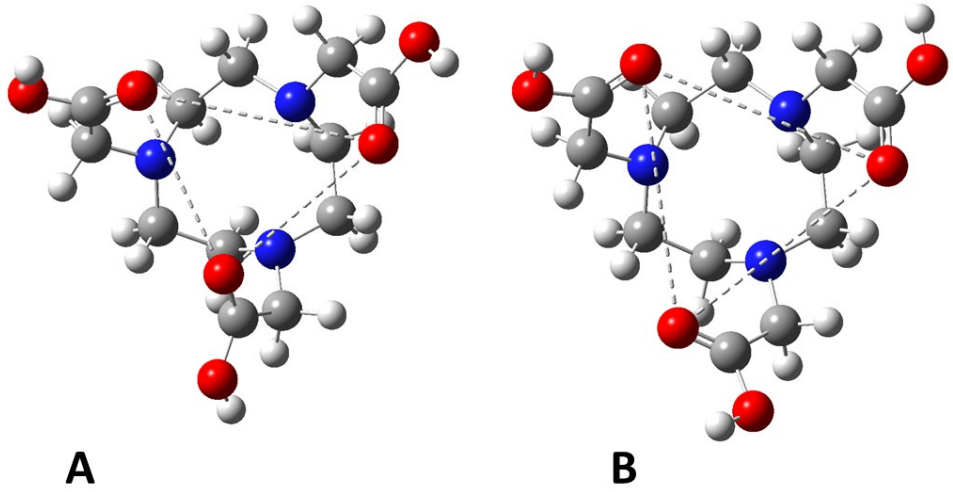

Figure 1S. The structures of free NOTA in A: vacuum and B: water media. The dotted lines show distances between carboxylic pendant arms of NOTA.

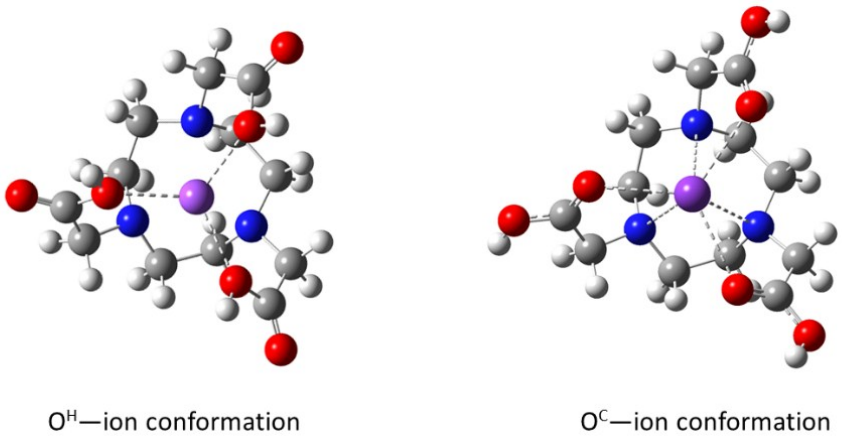

Figure 2S. The structures for O^{H}—ion and O^{C}—ion conformations.

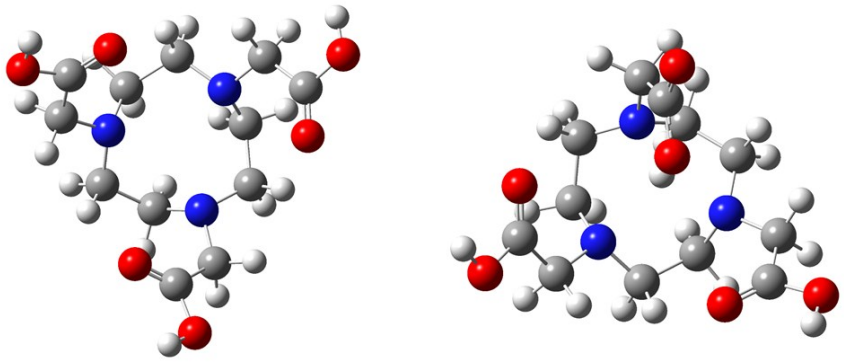

Figure 3S. The geometry optimized structures for free NOTA using B3LYP and ωB97XD functionals.

Table 1S. BSSE values for complexes of Li^+, Na^+, and K^+ ions using different basis set.

	BSSE			
Basis sets	6-31+G(d,p)	6-311G+(d,p)	6-311G+(2d,2p)	6-311G++(3d,3p)
Li^+	1.87	2.11	1.08	0.75
Na^+	2.31	2.05	1.42	1.25
K^+	1.01	0.69	0.55	0.49

Table 2S. BSSE of the different basis set used for complexes of Rb^+ ion.

Basis set	BSSE
6-31G+(d,p)/ LAN2DZ	0.44
6-311G+(d,p)/ LAN2DZ	0.35
6-311G+(2d,2p)/ LAN2DZ	0.34
6-311G++(3d,3p)/ LAN2DZ	0.40
6-311G++(3df,3dp)/ LAN2DZ	0.40
6-311G++(3df,3dp)/ LAN2MB	0.49
6-311G+(2d,2p)/Def2-TZVPD	0.28

Table 3S. Translational entropy contribution of the free ions and NOTA—ion complexes before calculation.

Ion/complex	Translational entropy
Li^+	31.80
Na^+	35.34
K^+	36.91
Rb+	39.23
NOTA—Li^+	43.09
NOTA—Na^+	43.24
NOTA—K^+	43.38
NOTA—Rb^+	43.76

Table 4S. Absolute values of the total entropy and vibrational contribution to entropy

Compounds	Total entropy (cal mol^{-1} K^{-1})		Vibrational entropy (cal mol^{-1} K^{-1})	
	Vacuum	Solvent	Vacuum	Solvent
NOTA	161.67	152.07	84.21	74.69
NOTA—Li^+	149.15	149.33	72.16	72.35
NOTA—Na^+	155.10	158.49	77.61	81.00
NOTA—K^+	159.29	162.55	81.35	84.58
NOTA—Rb^+	163.37	164.61	84.58	86.026

Table 5S. A Charge transfer from lone pairs of nitrogen atoms of NOTA to the ions.

Complexes	Donor	Acceptor	E^2(kcal/mol)
NOTA—Li^+	LP(N)	LP*(Li^+)	8.14 [11.43]
NOTA—Na^+	LP(N)	LP*(Na^+)	9.89 [5.48]
NOTA—K^+	LP(N)	LP*(K^+)	11.19 [3.32]
NOTA—Rb^+	LP(N)	LP*(Rb^+)	1.81 [2.34]

Table 6S. Proton NMR chemical shifts (δ) and natural atomic charges (NAC) of NOTA in vacuum and water media.

Proton	δ_{vacuum} (ppm)	$\delta_{solvent}$ (ppm)	NAC
G1	6.22	6.60	0.49
G2	4.93	4.88	0.20
G3	4.14	4.62	0.18
G4	3.45	3.47	0.16
G5	2.32	1.83	0.20
G6	1.31	0.21	0.18

Table 7S. The interaction energy values of NOTA—alkali metal complexes using B3LYP and ωB97XD functionals, with 6-311+G(2d,2p) basis sets.

Complexes	B3LYP E_{int} (kcal/mol)	ωB97XD E_{int} (kcal/mol)
NOTA—Li^+	-118.04	-107.69
NOTA—Na^+	-89.78	-77.40
NOTA—K^+	-64.01	-53.78
NOTA—Rb^+	-54.25	-46.59

Table 8S. The interatomic distances between alkali metals and heteroatoms of NOTA at the ωB97XD/6-311+G(2d,2p) level of theory for Li^+, Na^+ and K^+. The ωB97XD/Def2-TZVPD level of theory was used for NOTA—Rb^+ complex.

Complex	Average O-ion distance (≤ 3 Å)	Average N-ion distance (≤ 3 Å)
NOTA—Li^+	2.07	2.20
NOTA—Na^+	2.37	2.55
NOTA—K^+	2.72	2.92
NOTA—Rb^+	2.89	3.13