Electronic Supplementary Information

Inhibition of C(2)-H/D Exchange of a Bis(imidazolium) Dication Upon Complexation with Cucubit[7]uril

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Materials

Cucurbit[7]uril was synthesized by the reported method of Day *et al*.[1] The acetate and phosphate buffer solutions (total buffer concentration of 0.05 M for each kinetic experiment) were prepared by the requisite addition of DCl (Aldrich, 35 wt.% in D_2O) to D_2O solutions of sodium acetate and sodium phosphate (Aldrich), respectively. The ionic strength was adjusted to 0.2 M using NaCl.

Synthesis of [BMIX]Br_2:

α,α'-Bis(3-(1-methylimidazolium))-*p*-xylene was synthesized by using a modified literature method.[2] 1-methylimidazole (Aldrich, 1.0 g, 12 mmol) was heated with α,α'-dibromo-*p*-xylene (Aldrich, 1.58 g, 6.0 mmol) in THF under reflux for 36 hours to give an off-white precipitate. The crude product was filtered, washed with THF and ether, and dried in a vacuum oven to give a white power (2.4 g, 93% yield). M.p. 234-236 °C (dec.). ^{1}H NMR (D_2O, 400 MHz) δ 8.68 (s, 2H), 7.38 (br s, 8H), 5.34 (s, 4H), 3.80 (s, 6H) ppm. (Lit.[3] for [BMIX]I_2 ^{1}H NMR (DMSO-d_6) δ 9.20 (s, 2H, H_2), 7.75 (s, 2H, H_4), 7.70 (s, 2H, H_5), 7.45 (s, 4H, H_{Ar}), 5.41 (s, 4H, H_α), 3.84 (s, 6H, CH_3) ppm). ^{13}C NMR (D_2O, 100 MHz) δ 136.17, 134.60, 129.27, 123.87, 122.29, 52.30, 35.76 ppm. (Lit.[3] for [BMIX]I_2 ^{13}C NMR (D_2O, 100 MHz) δ 138.0, 134.8, 129.6, 124.1, 122.5, 52.6, 36.1 ppm). **ESI-MS:** *m/z* = 347.1 and 349.1 $[M\text{-}Br]^+$ (calc. 347.1 and 349.1), *m/z* = 267.2 $[M\text{-}2Br]^{2+}$ (calc. 267.2), shown in Fig. S1.

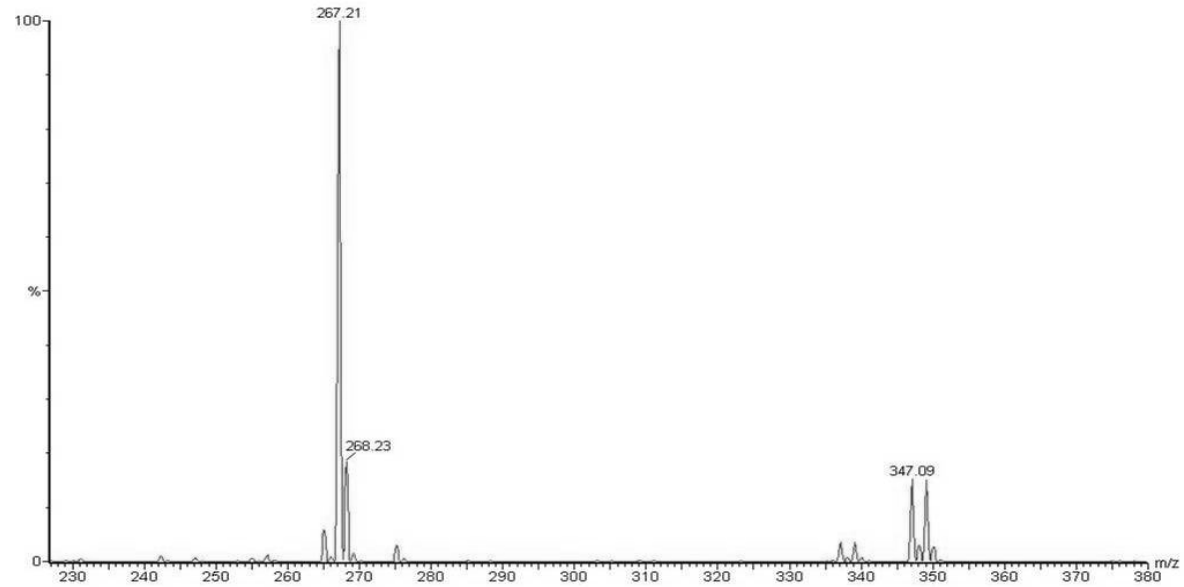

Fig. S1 Electrospray ionization mass spectrum of $[BMIX]Br_2$.

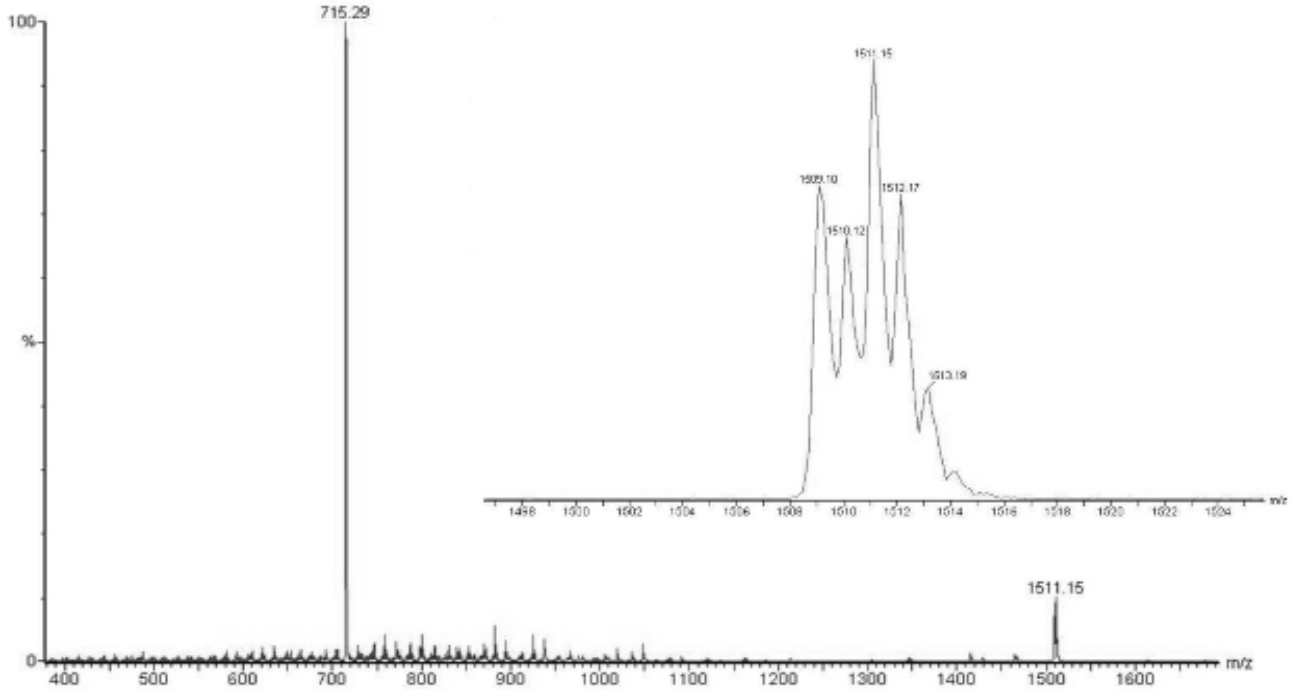

Fig. S2 Electrospray ionization mass spectrum of the $\{BMIX•CB[7]\}^{2+}$ guest-host complex. Single-charged peak observed at *m/z* = 1509 (calculated 1509) for $\{(BMIX+Br)•CB[7]\}^{+}$ (isotopic pattern shown enlarged in insert). Double-charged peak observed at *m/z* 715 (calculated 715) for $\{BMIX•CB[7]\}^{2+}$.

Determination of the Guest-Host Stability Constant:

The stoichiometry of the guest-host complex formed between $BMIX^{2+}$ and CB[7] was determined to be 1:1 based on a Job's plot (Fig. S3). The absorbance at 220 nm was monitored as the concentrations of CB[7] and $BMIX^{2+}$ were varied, keeping [CB[7]] + [$BMIX^{2+}$] = 1.0 mM. The maximum is located at [CB[7]]/([$BMIX^{2+}$] + [CB[7]]) = 0.50, indicating a 1:1 stoichiometry.

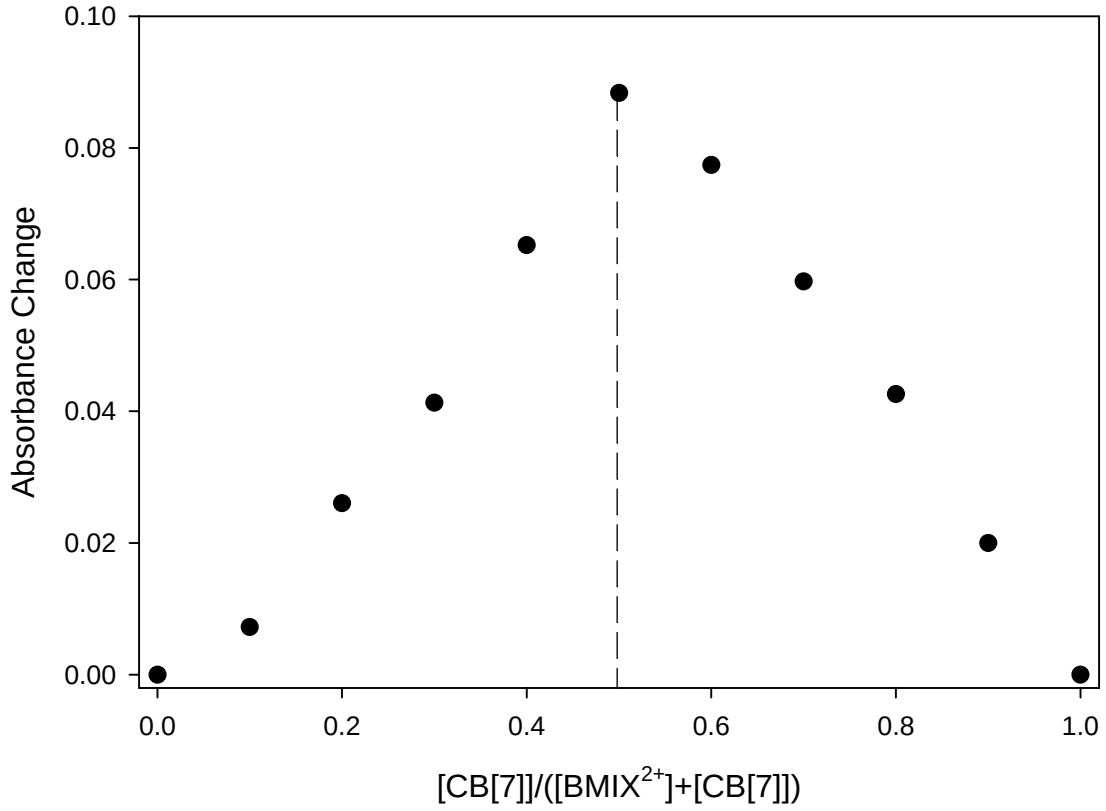

Fig. S3 Job's plot based on UV-visible continuous variation titration with [CB[7]] + [$BMIX^{2+}$] = 1.0 mM in aqueous solution, indicating a 1:1 complex formation between CB[7] and $BMIX^{2+}$.

The guest-host stability constant was estimated to be in the order of 10^8 -10^{10} M^{-1}, as a similar guest, the *p*-xylenediammonium dication was reported to have a binding constant with CB[7] of 1.84 x 10^9 M^{-1}. The (trimethylammonio)methylferrocene ($FcTMA^+$) cation

(as the iodide salt), with a binding constant with CB[7] of $(3.31 \pm 0.62) \times 10^{11}$ M^{-1},[4] was successfully employed as the competitor. The ^1H NMR spectrum of a D_2O (0.1 M NaCl) solution of 1.8 mM $FcTMA^+$ and 22.5 mM $BMIX^{2+}$, with a limiting quantity of CB[7] (about 2.1 mM) was recorded at 25 °C. The concentrations of the free and bound $BMIX^{2+}$ and $FcTMA^+$ were determined from integrations of their respective proton resonances (**Fig. S4**).

$[FcTMA^+]_{total}$ = 1.82 mM (integration for both bound and free trimethyl group protons is 9), $[CB[7]]_{total}$ = 1.82×15.60/14 = 2.03 mM (integration for 14 methylene protons of CB[7] is 15.60);

$[BMIX^{2+}]_{bound}$ = 1.82×1.58/4 = 0.72 mM (Integration for bound-guest 4 aromatic proton is 1.58);

$[BMIX^{2+}]_{free}$ = 1.82×(97.46-1.58)/8 = 21.81 mM (Integration for free-guest's four aromatic protons and the free and bound guest's four ethylene protons is 97.46, and with the integration of the four protons of the bound ethylene equaling 1.58);

Therefore, $[CB[7]\text{-}BMIX^{2+}]_{complex} = [BMIX^{2+}]_{bound}$ = 0.72 mM;

$[CB[7]\text{-}FcTMA^+]_{complex} = [CB[7]]_{total} - [CB[7]\text{-}BMIX^{2+}]_{complex}$ = 2.03 – 0.72 = 1.31 mM;

and $[FcTMA^+]_{free} = [FcTMA^+]_{total} - [CB[7]\text{-}FcTMA^+]_{complex}$ = 1.82 – 1.31 = 0.51 mM.

$K_{BMIX}/K_{FcTMA} = [CB[7]\text{-}BMIX^{2+}]_{complex} \times [FcTMA^+]_{free}/([CB[7]\text{-}FcTMA^+]_{complex} \times [BMIX^{2+}]_{free})$

= 0.72×0.51/(1.31×21.81) = 0.0128 and $K_{CB[7]\text{-}FcMA} = (3.31 \pm 0.62) \times 10^{11}$ M^{-1}

Therefore, $K_{BMIX} = (4.3 \pm 0.8) \times 10^9$ M^{-1}

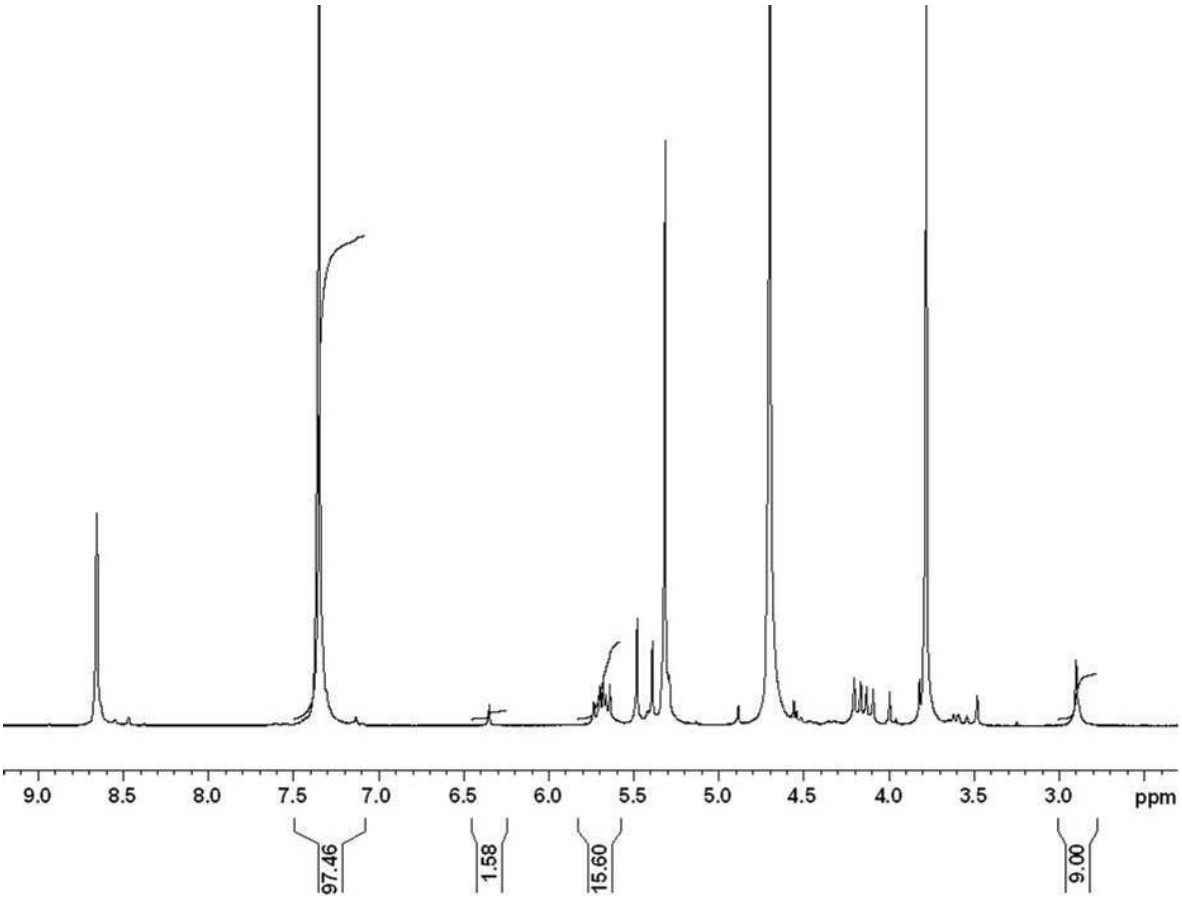

Fig. S4 ^{1}H NMR spectrum of the competition between $BMIX^{2+}$ (22.5 mM) and $FcTMA^{+}$ (1.8 mM) for CB[7] (2.1 mM,) in D_2O.

Kinetics of H/D exchange monitored by ^{1}H NMR spectroscopy:

Representative ^{1}H NMR spectra of $BMIX^{2+}$ in the absence and in the presence of CB[7] obtained during the hydrogen/deuterium exchange for the C(2)-proton at different p*D* conditions (buffered by $DOAc/OAc^{-}$ or $DPO_4/D_2PO_4^{-}$, or PO_4^{3-}/DPO_4^{2-} in D_2O, I = 0.20 (NaCl)) are given below. The xylyl methylene protons' resonance in $BMIX^{2+}$ is used as an internal reference resonance for obtaining the integration of the C(2)-protons. All of

the ^{1}H NMR spectra were recorded on an Avance 400MHz NMR spectrometer and, in order to acquire accurate integrals for the C(2)-proton resonance, a relaxation delay between pulses of d_1 = 75 s (> $5T_1$) was used.

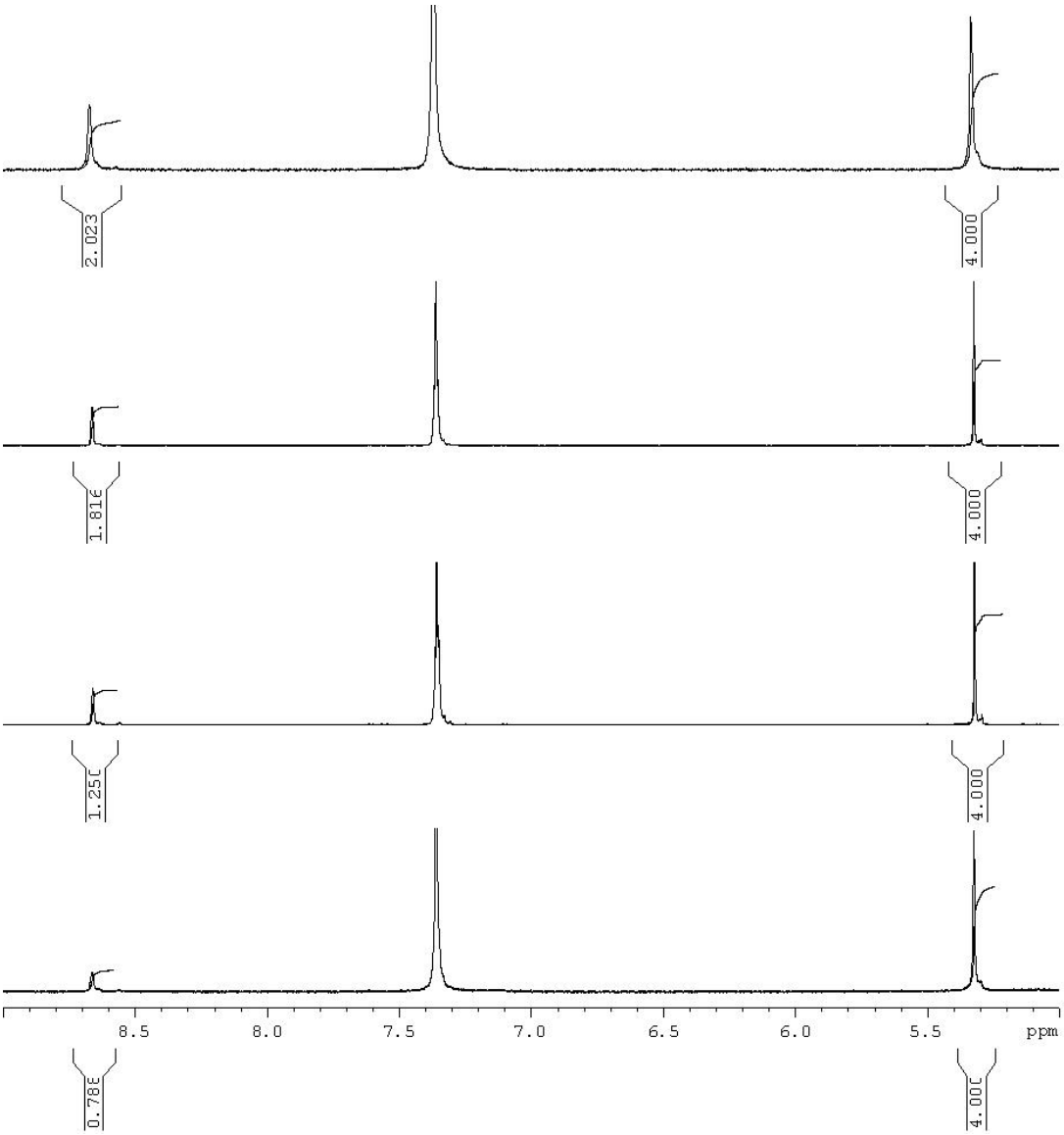

Fig. S5 Representative ^{1}H NMR spectra at 400 MHz of $BMIX^{2+}$ in the absence CB[7] obtained during deuterium exchange of C(2)-proton (in D_2O, p*D* = 5.2 buffered by $DOAc/OAc^-$, *I* = 0.2 (NaCl)). From top down, H/D exchange proceeded for 0, 4, 18, and 34 days.

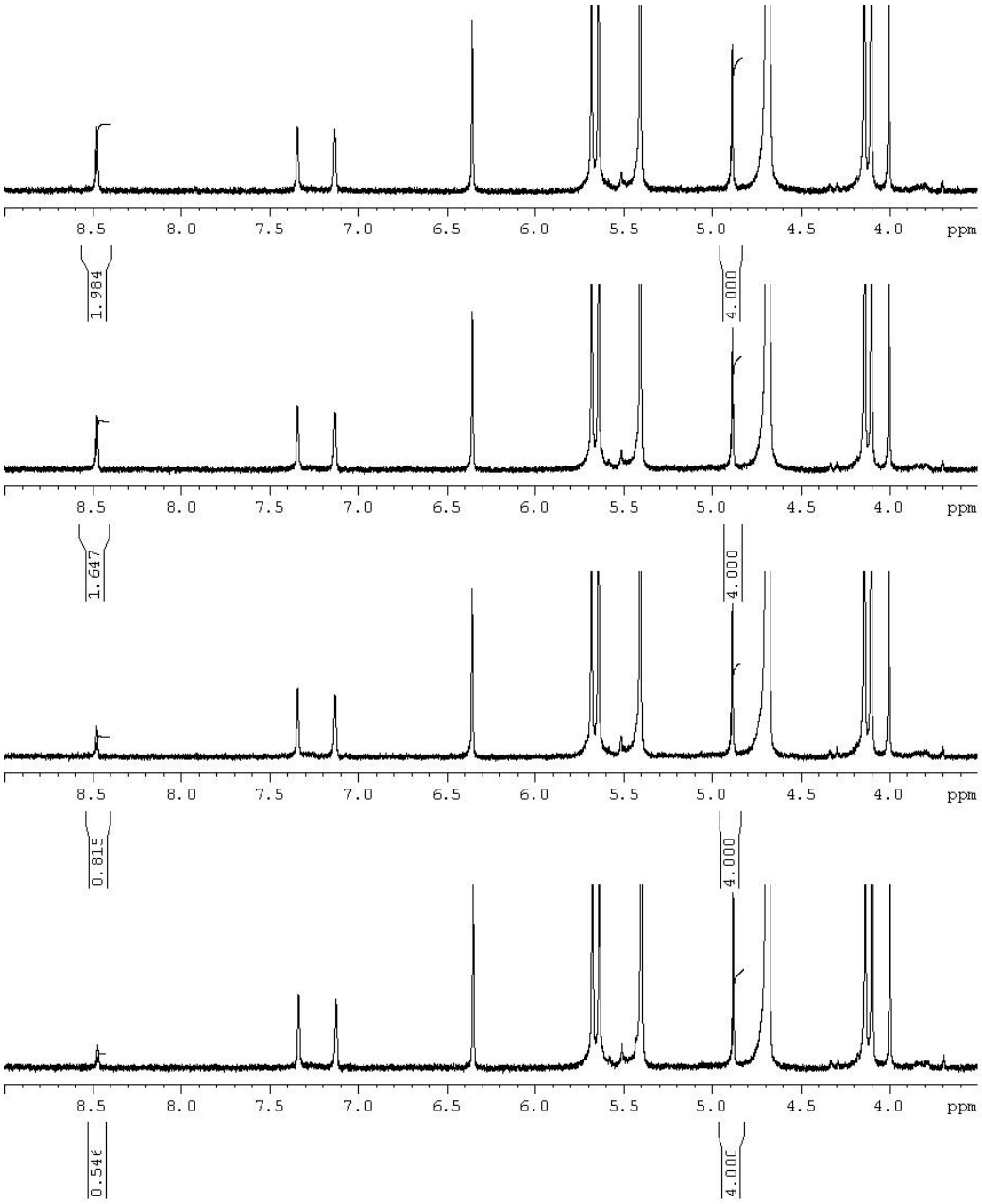

Fig. S6 Representative ^{1}H NMR spectra at 400 MHz of $BMIX^{2+}$ in the presence of 1.1 equiv. CB[7] obtained during deuterium exchange of C(2)-proton (in D_2O, p*D* = 9.5 buffered by $DPO_4^{2-}/D_2PO_4^{-}$, *I* = 0.2 (NaCl)). From top down, H/D exchange proceeded for 20 min, 7.5 hours, 2 days, and 3 days.

First-order rate constants determination by semilogarithmic plots:

Values of the reaction progress, *R*, were calculated from the integration of the resonances of C(2)-protons, compared with the internal reference of the methylene protons (H(α)), at zero time and time *t*, according to the equations below:

$R = (I_{2H})_t/((I_{2H})_0 = (I_{2H})_t/2$, as the reference methylene proton (H(α)) resonance integrated to four protons, and the initial integration for the C(2)-protons is two, relative to the four methylene (H(α)) protons;

$\ln R = -k_{ex}t$;

Therefore, the first-rate constants can be determined from the slopes of the linear semilogarithmic plots of reaction progress against reaction time (Fig. S7 and S8).

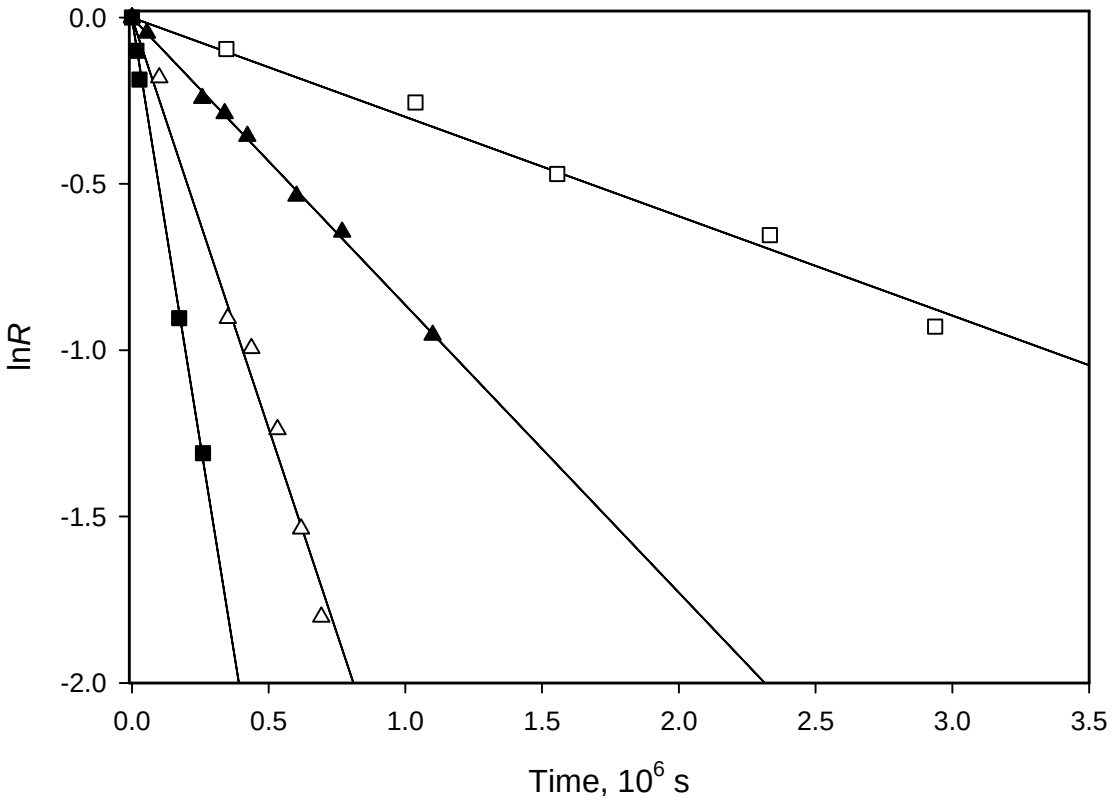

Fig. S7 Plots of ln*R* against time for the C(2)-H/D exchange reactions of $BMIX^{2+}$ at p*D* = 5.16 (□) and 6.17 (Δ) and $\{BMIX•CB[7]\}^{2+}$ at p*D* = 8.81 (▲) and 9.51 (■).

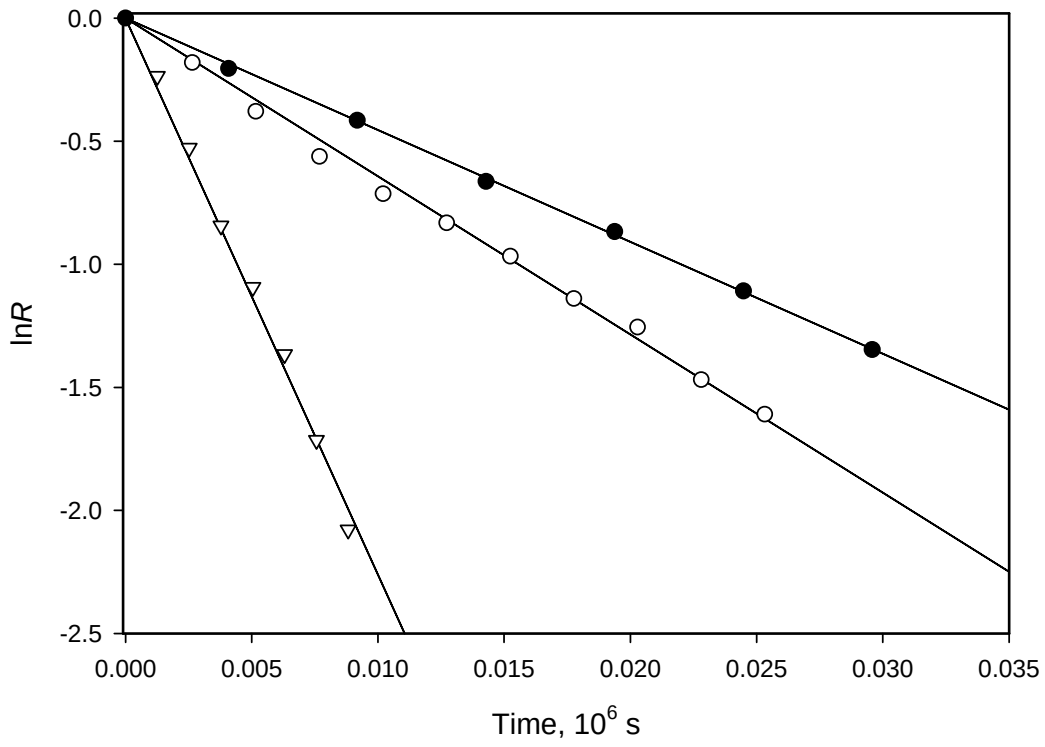

Fig. S8 Plots of ln*R* against time for the C(2)-H/D exchange reactions of $BMIX^{2+}$ at p*D* = 7.44 (○) and 8.07 (▽) and $\{BMIX•CB[7]\}^{2+}$ at p*D* = 10.15 (●).

Table S1. First-order rate constants, k_{ex}, for deuterium exchange of the C(2)-protons of $BMIX^{2+}$ in the absence and in the presence of 1.1 equiv of CB[7] in D_2O at 25 ˚C and I = 0.2 (NaCl) in various pD buffer solutions.

Species	10^3[Substrate] (M)	Buffer	pD	k_{ex} (s^{-1})
$BMIX^{2+}$	2.0	OAc^-/DOAc $f_B = 0.5$	5.16	2.98×10^{-7}
	2.0	OAc^-/DOAc $f_B = 0.9$	6.17	2.47×10^{-6}
	2.0	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.2$	7.44	6.43×10^{-5}
	2.0	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.8$	8.07	2.26×10^{-4}
$\{BMIX•CB[7]\}^{2+}$	0.5	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.9$	8.35	1.23×10^{-4}
	1.0	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.9$	8.44	1.15×10^{-5}
	5.0	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.9$	8.74	1.21×10^{-6}
	2.0	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.9$	8.81	8.64×10^{-7}
	2.0	$DPO_4^{2-}/D_2PO_4^-$ $f_B = 0.95$	9.51	5.11×10^{-6}
	2.0	PO_4^{3-}/DPO_4^{2-} $f_B = 0.1$	10.50	4.54×10^{-5}

Note: Total buffer concentration is 0.05 M in D_2O. f_B is the fraction of the base form of the buffer.

Determinations of the second-order rate constants:

The second-order rate constant, k_{OD}, is calculated from the y-axis intercept of the linear fits with a fixed slope of unity (**Fig. 3**) by using the first-order rate constants and pD conditions according to the equation below,[5]

$$\log k_{ex} = \log (k_{DO} K_W/\gamma_{OL}) + pD$$

where K_W = 14.87, and under our experimental conditions, the activity correction for deuterium oxide is $\gamma_{OL} = 0.83$.[5]

Ab Initio Energy-Minimized Calculations of the Structure of {BMIX•CB[7]}$^{2+}$

The structure of the {BMIX•CB[7]}$^{2+}$ guest-host complex was computed by energy minimizations using Gaussian 03, Revision C.02 programs[6] run on the computing facilities of the High Performance Virtual Computing Laboratory (HPVCL) at Queen's University. The structure of the complex was originally constructed using ChemDraw and Chem 3D (ChemOffice 7.0, CambridgeSoft) programs and imported into Gaussian 03. The basis set used for the calculations was HF/3-21G**. The structure was minimized to final energy of -4995.49632663 A.U. A picture of the guest-host complex, with the Cartesian axes added, is given in Figure S9. The Cartesian coordinates of the atoms are given in Table S2.

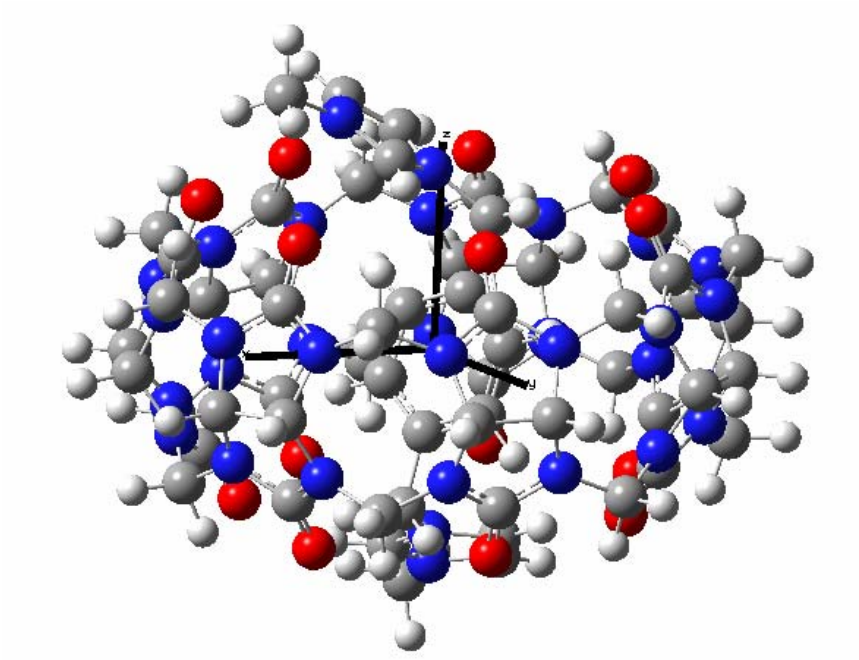

Fig. S9 A "ball and bond" picture of the energy-minimized structure of {BMIX •CB[7]}$^{2+}$ showing the Cartesian axes (z is vertical and y points to the right).

Table S2. Coordinates of the atoms in energy-minimized structure of $\{BMIX•CB[7]\}^{2+}$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.164528	-4.020472	0.733153
2	6	0	-2.916710	-4.988775	0.674664
3	7	0	-2.070802	-4.484570	1.730725
4	6	0	-2.572476	-3.357731	2.333589
5	7	0	-3.814555	-3.120560	1.806112
6	7	0	-4.189048	-3.445101	-0.595117
7	6	0	-3.182779	-3.909140	-1.403407
8	7	0	-2.425433	-4.794791	-0.672500
9	8	0	-2.052205	-2.739964	3.241083
10	8	0	-3.044172	-3.660304	-2.583830
11	6	0	0.614558	-5.779890	0.322976
12	6	0	2.138582	-5.422393	0.096854
13	7	0	2.456807	-4.607937	1.246321
14	6	0	1.369631	-4.367346	2.052146
15	7	0	0.303680	-5.060411	1.534800
16	7	0	-0.018658	-5.289200	-0.886053
17	6	0	0.856247	-4.654188	-1.726719
18	7	0	2.108504	-4.730175	-1.174062
19	8	0	1.371566	-3.728551	3.082465
20	8	0	0.595567	-4.181557	-2.818054
21	6	0	-0.930945	-5.188404	2.280699
22	6	0	-1.384137	-5.592568	-1.289133
23	6	0	4.914930	-3.105181	-0.371371
24	6	0	5.553445	-1.667676	-0.522426
25	7	0	5.267472	-1.054574	0.755838
26	6	0	4.562591	-1.872556	1.606201
27	7	0	4.350829	-3.066104	0.958794
28	7	0	3.958660	-3.142937	-1.456225
29	6	0	3.878812	-1.961388	-2.147181
30	7	0	4.842400	-1.120608	-1.658952
31	8	0	4.263984	-1.622723	2.755296
32	8	0	3.127864	-1.737894	-3.081675
33	6	0	5.503408	1.964940	-0.635965
34	6	0	4.803956	3.382893	-0.582780
35	7	0	4.125282	3.345149	0.697281
36	6	0	4.350861	2.192168	1.399009
37	7	0	5.196110	1.404381	0.661579
38	7	0	4.848221	1.336809	-1.760828
39	6	0	3.940970	2.156532	-2.389112
40	6	0	-0.268100	0.730846	1.218058
41	6	0	0.446963	-0.360945	0.738088
42	6	0	0.781709	-0.443063	-0.603528
43	6	0	0.411536	0.562501	-1.485248
44	6	0	-0.305822	1.640579	-1.007521
45	6	0	-0.639843	1.726322	0.332592
46	6	0	-0.670964	0.858308	2.682928
47	7	0	0.395838	0.332544	3.559388
48	6	0	0.725986	0.486802	-2.966917
49	7	0	-0.274307	-0.395183	-3.618387
50	6	0	1.509444	0.979725	3.875794
51	7	0	2.267922	0.171206	4.595778

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
52	6	0	1.622021	-1.057857	4.725804
53	6	0	0.447040	-0.957412	4.086890
54	6	0	-1.638772	-0.130066	-3.737432
55	6	0	-2.187467	-1.215929	-4.303461
56	7	0	-1.156217	-2.124470	-4.536239
57	6	0	-0.023434	-1.603872	-4.092968
58	6	0	3.619625	0.460319	5.120797
59	6	0	-1.324737	-3.462904	-5.139041
60	1	0	-0.448305	-4.043858	-4.916282
61	1	0	-1.460856	-3.361601	-6.204693
62	1	0	-2.181997	-3.917747	-4.677956
63	1	0	3.595466	0.419956	6.198501
64	1	0	3.916772	1.433314	4.777643
65	1	0	4.285658	-0.281019	4.716085
66	1	0	-3.201164	-1.442451	-4.507419
67	1	0	2.074207	-1.880911	5.216892
68	1	0	0.925535	-2.081094	-4.061347
69	1	0	-2.077502	0.779310	-3.405028
70	1	0	-0.332256	-1.661439	3.919946
71	1	0	1.745160	1.968698	3.561976
72	1	0	1.693726	0.064923	-3.156665
73	1	0	0.676546	1.461920	-3.418423
74	1	0	-0.611031	2.394612	-1.695266
75	1	0	1.324610	-1.290705	-0.966343
76	1	0	-1.569008	0.304340	2.900663
77	1	0	-0.846668	1.888303	2.938515
78	1	0	-1.174322	2.581281	0.678896
79	1	0	0.750306	-1.137644	1.409012
80	7	0	3.951325	3.367023	-1.745360
81	8	0	3.948307	1.957027	2.523710
82	8	0	3.314867	1.879882	-3.389419
83	6	0	5.812354	0.211373	1.210331
84	6	0	5.242453	0.083470	-2.367914
85	6	0	3.792339	-4.211297	1.653914
86	6	0	3.285663	-4.340221	-1.922372
87	6	0	1.890440	5.578378	-0.381028
88	6	0	0.339525	5.868636	-0.282169
89	7	0	-0.025318	5.245335	0.972164
90	6	0	1.010019	4.553355	1.553085
91	7	0	2.139705	4.794058	0.810797
92	7	0	2.004440	4.863130	-1.630183
93	6	0	0.792523	4.604748	-2.218151
94	7	0	-0.178421	5.223421	-1.467701
95	8	0	0.957807	3.916809	2.589317
96	8	0	0.609329	3.998118	-3.252780
97	6	0	-3.176362	5.042248	-0.026659
98	6	0	-4.420842	4.070773	0.096332
99	7	0	-4.232358	3.477058	1.398430
100	6	0	-3.053701	3.837017	1.996618
101	7	0	-2.430299	4.752902	1.182027
102	7	0	-2.552060	4.608302	-1.253614
103	6	0	-3.139003	3.488106	-1.791860
104	7	0	-4.240641	3.180529	-1.036276

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
105	8	0	-2.650942	3.466615	3.079270
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108	6	0	-1.533461	5.352427	-1.972657
109	6	0	3.460905	4.477456	1.313963
110	6	0	3.247415	4.513684	-2.289697
111	6	0	-5.238982	2.241543	-1.527433
112	6	0	-5.173850	2.598872	2.064011
113	6	0	-5.267965	-2.625600	-1.127647
114	6	0	-4.740100	-2.207545	2.446167
115	6	0	-5.859067	-0.818751	0.599350
116	6	0	-5.934431	0.752846	0.439010
117	7	0	-5.198292	1.230818	1.584311
118	7	0	-4.986933	-0.969476	1.741871
119	7	0	-5.313863	-1.249934	-0.669046
120	6	0	-4.964986	-0.202805	-1.489907
121	7	0	-5.301135	0.964217	-0.846099
122	6	0	-4.577063	0.224635	2.279305
123	8	0	-4.528994	-0.292397	-2.618726
124	8	0	-3.861894	0.357881	3.250113
125	1	0	-5.094706	-4.524034	0.946520
126	1	0	-3.162926	-6.025444	0.845570
127	1	0	0.429189	-6.835872	0.442874
128	1	0	2.784857	-6.284739	0.045925
129	1	0	-1.183223	-6.237816	2.358663
130	1	0	-0.743804	-4.778337	3.258486
131	1	0	-1.446828	-5.417252	-2.348721
132	1	0	-1.571688	-6.636251	-1.074537
133	1	0	5.627088	-3.910189	-0.463937
134	1	0	6.615427	-1.681184	-0.711621
135	1	0	6.570763	2.011804	-0.786204
136	1	0	5.494525	4.210630	-0.623161
137	1	0	6.867884	0.238275	0.975585
138	1	0	5.670254	0.242336	2.276266
139	1	0	4.776088	0.052444	-3.338158
140	1	0	6.319567	0.067356	-2.471920
141	1	0	3.734296	-3.938813	2.694099
142	1	0	4.455620	-5.055787	1.523026
143	1	0	2.965119	-4.155047	-2.932689
144	1	0	3.995715	-5.156041	-1.902432
145	1	0	2.501869	6.466887	-0.387275
146	1	0	0.092187	6.918541	-0.271712
147	1	0	-3.443141	6.086282	-0.077071
148	1	0	-5.372807	4.574058	0.036973
149	1	0	-1.490460	6.550972	1.607243
150	1	0	-1.139746	5.196457	2.692685
151	1	0	-1.518458	4.973960	-2.981107
152	1	0	-1.810174	6.398177	-1.966035
153	1	0	4.087479	5.351104	1.190975
154	1	0	3.357942	4.244284	2.359336
155	1	0	2.997312	4.269093	-3.308429
156	1	0	3.908641	5.368534	-2.258782
157	1	0	-4.994455	2.030936	-2.554888

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
158	1	0	-6.208757	2.718062	-1.465321
159	1	0	-4.880040	2.563963	3.099594
160	1	0	-6.166581	3.015057	1.967280
161	1	0	-5.131800	-2.598309	-2.195101
162	1	0	-6.210020	-3.098076	-0.883510
163	1	0	-4.312136	-1.940504	3.397832
164	1	0	-5.681288	-2.722917	2.588740
165	1	0	-6.815900	-1.283463	0.780485
166	1	0	-6.940397	1.142613	0.439880

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