Supporting Information for

Guided Ion Beam and Theoretical Studies of Sequential Bond Energies of Water to Sodium Cysteine Cation

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Table S1 provides the relative theoretical 0 K enthalpies and 298 K free energies (kJ/mol) for $Na^+Cys(H_2O)_x$ (x = 1 – 4) optimized at the B3LYP/6-311+G(d,p) level with single point energies calculated using the 6-311+G(2d,2p) basis set and the indicated level of theory. Table S2 provides the geometrical parameters of these same complexes. Ground state species are indicated by bold face.

Figure S1 shows structures of $Na^+Cys(H_2O)_x$ (x = 1 – 4) complexes calculated at the B3LYP/6-311+G(d,p) level of theory. Relative 0 K energies in kJ/mol from single point energy calculations including zero point energies taken from Table S1 are indicated. Hydrogen bonds in Ångstroms are shown. (H – white; C – grey; N – blue; O – red; Na – purple; S – yellow)

Table S1. Relative theoretical 0 K enthalpies (298 K free energies) in kJ/mol of $Na^+Cys(H_2O)_x$ [a]

x	Structure	ΔΔG[b]	B3LYP	B3P86	MP2(full)
0	**[N,CO,S]-tggg$_+$**		**0.0 (0.0)**	**0.0 (0.0)**	**0.0 (0.0)**
	[N,CO,S]-tggg$_-$		4.6 (4.4)	3.4 (3.2)	4.1 (3.9)
	[CO_2^-]-ctgg$_+$		11.1 (9.3)	7.1 (5.2)	11.6 (9.8)
	[CO_2^-]-ctgg$_-$		15.0 (12.5)	11.2 (8.6)	16.8 (14.3)
	[N,CO]-tcgg		15.3 (13.2)	14.4 (12.2)	16.4 (14.3)
	[N,OH,S]-tggg$_+$		30.6	31.9	27.2
	TS[CO_2^-/COOH]-ctgg$_+$		26.4	17.2	27.5
	[COOH]-ctgg$_-$		26.9	22.8	27.8
	[COOH]-ctgg$_+$		27.4	22.8	28.4
	TS[CO_2^-/COOH]-ctgg$_-$		27.8	18.7	29.7
	[CO,S]-ctgt		23.7	21.5	31.6
1	**1W[N,CO,S]-tggg$_+$**	4.2	**0.0 (0.0)**	**0.0 (0.0)**	**0.0 (0.0)**
	1W[N,CO,S]-tggg$_-$	4.6	3.2 (3.6)	3.5 (3.9)	4.6 (5.0)
	1W[CO_2^-]-ctgg$_+$	2.3	8.9 (6.1)	4.9 (2.1)	11.9 (9.1)
	1W[N,CO]-tcgg	1.7	10.0 (7.5)	9.8 (7.3)	13.2 (10.8)
	1W[N,CO]-tgtg	3.1	13.0 (11.9)	12.6 (11.5)	17.0 (15.9)
	1W[bO^-]-[CO_2^-]-ctgg$_+$	11.9	15.6 (23.4)	9.2 (16.9)	17.9 (25.6)
	1W[CO_2^-]-ctgg$_-$	2.1	13.6 (11.5)	9.7 (7.6)	17.9 (15.8)
	1W[HO]-[N,CO,S]-tggg$_+$	10.0	18.1 (23.9)	13.4 (19.2)	18.9 (24.7)
	1W[COOH]-ctgg$_+$	0.0	17.7 (13.6)	13.7 (9.5)	21.8 (17.6)
	1W[bO^-]-[CO_2^-]-cgtg	10.5	18.7 (25.8)	13.6 (20.7)	22.8 (29.8)
	TS-1W[CO_2^-/COOH]-ctgg$_+$	1.6	19.3 (16.7)	10.3 (7.7)	23.1 (20.5)
	1W[bCO]-[CO_2^-]-ctgg$_+$	10.7	21.4 (28.0)	15.4 (22.0)	23.3 (29.9)
	1W[bOH]-[CO]-ctgg$_-$	7.7	22.5 (26.0)	17.7 (21.2)	25.5 (29.0)
	1W[bOH]-[CO]-ctgg$_+$	9.3	22.8 (27.9)	17.4 (22.6)	26.0 (31.1)
	1W[HN]-[CO_2^-]-ctgg$_+$	5.6	29.1 (30.5)	21.8 (23.2)	28.8 (30.1)
	1W[bO^-]-[CO_2^-]-cggg	11.2	40.0 (46.4)	35.3 (41.7)	44.2 (50.6)

Table S1. continued

x	Structure	ΔΔG[b]	B3LYP	B3P86	MP2(full)
2	**2W[N,CO,S]-tggg$_+$**	7.6	**0.0 (0.0)**	5.9 (3.4)	**0.0 (0.0)**
	2W[N,CO,S]-tggg$_-$	8.3	6.0 (6.7)	9.9 (8.1)	5.3 (6.0)
	2W[HO]-[N,CO,S]-tggg$_+$	9.6	0.7 (2.7)	2.6 (2.1)	6.1 (8.0)
	2W[bO$^-$]-[CO$_2$$^-$]-ctgg$_+$	11.3	0.0 (3.7)	**0.0** (1.2)	8.3 (12.0)
	2W[N,CO]-tcgg	9.0	3.5 (4.9)	9.8 (8.7)	9.8 (11.2)
	2W[bOH]-[CO]-ctgg$_+$	8.2	1.9 (2.4)	3.3 (1.4)	11.1 (11.7)
	2W[bOH]-[CO]-ctgg$_-$	6.2	1.9 (0.4)	4.0 **(0.0)**	11.3 (9.8)
	2W[bO$^-$]-[CO$_2$$^-$]-cgtg	10.3	3.5 (6.2)	4.8 (5.0)	13.8 (16.4)
	2W[bO$^-$]-[CO$_2$$^-$]-ctgg$_-$	10.6	4.8 (7.8)	5.1 (5.6)	14.4 (17.4)
	2W[bCO]-[CO$_2$$^-$]-ctgg$_+$	10.3	6.3 (9.0)	6.6 (6.8)	14.4 (17.1)
	TS-2W[bO$^-$/bOH]-[CO$_2$$^-$/CO]-ctgg$_+$	11.5	6.0 (9.9)	1.9 (3.4)	14.8 (18.7)
	2W[HN]-[CO$_2$$^-$]-ctgg$_+$	3.1	8.6 (4.1)	7.8 (0.8)	15.3 (10.8)
	2W[bOH]-[CO]-cgtg	7.6	5.5 (5.5)	7.6 (5.1)	15.8 (15.9)
	TS-2W[bO$^-$/bOH]-[CO$_2$$^-$/CO]-ctgg$_-$	8.7	8.5 (9.6)	4.6 (3.2)	18.2 (19.3)
	2W[bOH,bS]-[CO]-ctgt	14.4	14.0 (20.9)	14.7 (19.1)	20.0 (26.8)
	2W[HN,bO$^-$]-[CO$_2$$^-$]-ctgg$_+$	13.2	15.3 (20.8)	11.9 (14.9)	21.2 (26.8)
	2W[HN]-[CO$_2$$^-$]-ctgg$_-$	3.4	14.1 (9.9)	13.6 (6.9)	22.3 (18.1)
	2W[bO$^-$]-[CO$_2$$^-$]-cggg	9.0	24.0 (25.4)	24.9 (23.8)	33.6 (35.0)
	2W[HN,bO$^-$]-[CO$_2$$^-$]-ctgg$_-$	12.0	19.9 (24.9)	16.8 (18.7)	26.9 (31.3)
	2W[bO$^-$,bS]-[CO$_2$$^-$]-cggt	15.9	31.8 (40.1)	30.7 (36.4)	35.7 (44.0)
	2W[HN]-[COOH]-ctgg$_+$	0.0	36.7 (29.1)	35.3 (25.2)	44.4 (36.8)
	2W[HN,bO$^-$]-[CO$_2$$^-$]-cggg$_-$	11.7	37.5 (41.6)	36.0 (37.6)	45.2 (49.4)
	2W[HN,bOH]-[CO]-ctgg$_+$	9.9	42.2 (44.5)	38.7 (38.5)	48.8 (51.1)

Table S1. continued

x	Structure	ΔΔG[b]	B3LYP	B3P86	MP2(full)
3	**3W[bOH,bS]-[CO]-ctgt**	11.2	**0.0** (9.4)	3.0 (9.1)	**0.0** (6.2)
	3W[HO,bCO]-[N,CO,S]-tggg$_+$	4.0	4.6 (6.6)	7.7 (6.4)	1.2 **(0.0)**
	3W[bOH]-[CO]-ctgg$_+$	1.2	0.6 **(0.0)**	3.9 **(0.0)**	4.4 (0.6)
	3W[HN,bO$^-$]-[CO_2^-]-ctgg$_+$	5.9	1.6 (5.9)	**0.0** (1.0)	5.9 (7.0)
	3W[bO$^-$,bW]-[CO_2^-]-ctgg$_+$	11.9	4.9 (15.0)	5.4 (12.2)	7.2 (14.1)
	3W[bS,bCO,bW]-[N,CO]-tggg$_+$	11.5	12.2 (21.9)	18.4 (24.8)	7.4 (13.9)
	3W[bS,bCO,bW]-[N,CO]-tggt	10.9	15.8 (25.0)	21.6 (27.4)	8.0 (13.9)
	3W[HO,bS]-[N,CO]-tggg$_+$	7.8	7.0 (13.0)	9.7 (12.4)	8.6 (11.4)
	3W[bOH]-[CO]-cgtg	3.5	4.4 (6.1)	8.7 (7.1)	9.8 (8.2)
	3W[HN,bCO]-[CO_2^-]-ctgg$_+$	4.7	7.2 (10.1)	5.8 (5.4)	11.0 (10.6)
	TS-3W[bOH/bO$^-$,bW]-[CO/CO_2^-]-ctgg$_+$	10.4	9.1 (17.6)	5.7 (11.0)	11.6 (16.9)
	TS-3W[bOH/bO$^-$,bS/bW]-[CO/CO_2^-]-ctgt	12.8	13.5 (24.5)	10.9 (18.6)	12.5 (20.3)
	3W[bO$^-$,bW]-[CO_2^-]-cgtg	10.9	8.9 (18.0)	10.4 (16.2)	13.2 (19.1)
	3W[bOH]-[CO]-cgtt	0.0	7.9 (6.1)	11.8 (6.7)	13.8 (8.7)
	3W[bOH,bW]-[CO]-ctgg$_-$	10.8	10.3 (19.4)	10.4 (16.1)	13.9 (19.6)
	3W[bO$^-$,bW]-[CO_2^-]-ctgg$_-$	11.6	10.3 (20.1)	10.6 (17.1)	14.0 (20.6)
	3W[HN,bCO]-[CO_2^-]-ctgg$_-$	3.7	14.2 (16.1)	12.4 (11.0)	19.1 (17.7)
	TS-3W[HN,bO$^-$/bOH]-[CO_2^-/CO]-ctgg$_+$	4.3	19.8 (22.3)	14.6 (13.8)	24.9 (24.2)
	3W[HN,bOH]-[CO]-ctgg$_+$	1.1	22.4 (21.7)	21.8 (17.7)	27.8 (23.8)
	3W[bO$^-$,bS]-[CO_2^-]-cggg	11.0	27.6 (36.8)	29.1 (34.9)	28.7 (34.6)
	3W[HNf,bO$^-$]-[CO_2^-]-cggg	5.9	23.4 (27.5)	23.6 (24.4)	29.6 (30.4)
	3W[HNr,bO$^-$]-[CO_2^-]-cggg	4.9	25.8 (28.9)	25.5 (25.2)	30.6 (30.4)
	3W[bO$^-$,bW]-[CO_2^-]-cggg	10.5	28.2 (36.9)	30.4 (35.8)	32.4 (37.8)

Table S1. continued

x	Structure	$\Delta\Delta G^{b}$	B3LYP	B3P86	MP2(full)
4	**4W[HN,bO$^-$,bW]-[CO_2^-]-ctgg$_+$**	**7.9**	**0.0 (0.0)**	**0.0 (0.0)**	**0.0 (0.0)**
	4W[bOH,AA]-[CO]-ctgg$_+$	10.2	0.2 (2.5)	3.4 (5.7)	2.0 (4.3)
	4W[HN-bW,bO$^-$,AD]-[CO_2^-]-cgtg$_-$	18.7	9.7 (20.5)	7.9 (18.7)	4.1 (15.0)
	4W[HO,bS,bCO,bW]-[N,CO]-tggg$_+$	12.3	11.3 (15.7)	15.8 (20.2)	4.8 (9.2)
	4W[HN,bO$^-$,bW]-[CO_2^-]-cgtg$_-$	7.7	4.4 (4.3)	5.1 (4.9)	5.8 (5.7)
	4W[HN-bO$^-$r,bO$^-$,bWr]-[CO_2^-]-cgtg$_-$	12.7	9.2 (14.0)	10.2 (15.0)	6.1 (10.9)
	4W[HN-bO$^-$f,bO$^-$,bWf]-[CO_2^-]-cgtg$_-$	12.1	9.1 (13.3)	9.8 (13.9)	6.4 (10.6)
	4W[bOH,AA]-[CO]-cgtg$_-$	9.7	4.3 (6.2)	7.4 (9.3)	6.8 (8.6)
	4W[HN,bO$^-$,bW]-[CO_2^-]-ctgg$_-$	7.5	5.9 (5.6)	6.3 (5.9)	7.5 (7.1)
	4W[bO$^-$,AA]-[CO_2^-]-ctgg$_+$	11.9	6.6 (10.6)	7.7 (11.7)	7.5 (11.5)
	4W[bS,bCO,bHN,bW]-[N,CO]-tggg$_+$	18.5	23.0 (33.6)	27.8 (38.4)	7.8 (18.5)
	4W[HN-bW,bO$^-$,AD]-[CO_2^-]-cgtg$_+$	17.6	13.8 (23.5)	12.3 (22.0)	8.5 (18.2)
	4W[HN-bS,bO$^-$,bW]-[CO_2^-]-cgtg$_-$	9.4	10.7 (12.2)	10.7 (12.3)	8.9 (10.4)
	4W[bS,bOH,AD]-[CO]-ctgt	16.4	11.3 (19.8)	13.7 (22.1)	9.0 (17.4)
	4W[HO,bS,bW]-[N,CO]-tggt	7.7	18.4 (18.2)	21.4 (21.2)	9.1 (8.9)
	TS-4W[bOH/bO$^-$,AA]-[CO/CO_2^-]-ctgg$_+$	13.0	8.1 (13.2)	5.5 (10.5)	9.5 (14.6)
	4W[HN,bO$^-$,bW]-[CO_2^-]-cgtt	6.5	7.7 (6.3)	8.6 (7.3)	9.8 (8.4)
	4W[AA-bCO]-[CO_2^-]-ctgg$_+$	14.8	11.1 (18.0)	12.1 (18.9)	9.8 (16.7)
	4W[HO-bCO,bW,AD]-[N,CO]-tggg$_+$	10.7	15.3 (18.0)	18.2 (21.0)	10.5 (13.3)
	4W[HN-bO$^-$,bO$^-$,bW]-[CO_2^-]-cgtg$_+$	10.9	12.9 (15.9)	14.3 (17.3)	11.1 (14.1)
	4W[AA-bO$^-$]-[CO_2^-]-cgtg$_-$	11.6	10.4 (14.1)	12.4 (16.1)	11.2 (14.9)
	4W[HN-bS,bO$^-$,bW]-[CO_2^-]-cgtt	10.9	13.3 (16.3)	13.0 (16.0)	13.4 (16.4)
	4W[bOH,AD-CO]-[CO]-ctgt	5.9	16.1 (14.0)	18.9 (16.8)	13.4 (11.4)
	4W[bO$^-$,AA]-[CO_2^-]-cgtg$_-$	11.1	10.6 (13.8)	13.2 (16.4)	13.9 (17.1)

Table S1. continued

x	Structure	ΔΔG[b]	B3LYP	B3P86	MP2(full)
	4W[bOH,AA]-[CO]-cgtt	7.3	11.3 (10.7)	13.2 (12.6)	13.9 (17.1)
	4W[AA-bN]-[CO]-tggg	19.6	22.5 (34.2)	23.7 (35.4)	15.5 (27.2)
	TS-4W[HN,bO$^-$/bOH,bW]-[CO_2^-/CO]-ctgg$_+$	5.5	16.3 (13.9)	13.4 (11.0)	16.9 (14.5)
	4W[HN,bOH]-[CO]-ctgg$_+$	0.0	15.8 (7.8)	18.8 (10.9)	17.6 (9.7)
	4W[bO$^-$,bW,AD]-[CO_2^-]-cgtg$_-$	18.0	17.0 (27.0)	14.6 (24.6)	17.6 (27.7)
	4W[AA-bCO]-[CO_2^-]-ctgg$_-$	14.0	17.5 (23.6)	17.9 (24.0)	17.6 (23.7)
	4W[bO$^-$,AD-CO]-[CO_2^-]-ctgt	10.6	23.4 (26.0)	21.6 (24.3)	18.0 (20.7)

[a] Structures optimized at the B3LYP/6-311+G(d,p) level and all single point energies are calculated using the 6-311+G(2d,2p) basis set and the indicated level of theory. Ground state species are indicated by bold face.

[b] Relative $\Delta G_{298} - \Delta H_0$ (kJ/mol).

Table S2. Geometrical parameters of $Na^+Cys(H_2O)_x$ structures optimized at B3LYP/6-311+G(d,p).

Species[a]	$r(Na^+-O=C)$ (Å)	$r(Na^+-OH_2)$ (Å)	$\angle Na^+-O=C$ (°)	$\angle Na^+-O=C-C$ (°)	$\angle N-C-C=O$ (°)	$\angle C=O-Na^+-OH_2$ Dihedral (°)
[N,CO,S]-tggg$_+$	2.308		112.2	-14.5	-25.2	
[CO_2^-]-ctgg$_+$	2.293, 2.324		88.7, 86.8	-175.0, 175.0	-166.7, 15.1	
[N,CO]-tcgg$_+$	2.236		119.6	1.4	12.7	
[N,OH,S]-tggg$_+$[b]	2.386		112.6	-24.2	-19.9	
[COOH]-ctgg$_-$	2.285		98.1	178.6	-171.7	
[CO,S]-ctgt	2.162		129.7	86.7	-161.3	
1W[N,CO,S]-tggg$_+$	2.340	2.279	112.8	-15.7	-23.5	174.0
1W[N,CO,S]-tggg$_-$	2.315	2.280	113.6	-14.0	-24.7	175.6
1W[CO_2^-]-ctgg$_+$	2.320, 2.357	2.270	89.0, 86.7	-174.8, 174.9	-166.5, 15.2	177.7
1W[N,CO]-tcgg	2.266	2.270	120.0	1.8	13.4	176.4
1W[N,CO]-tgtg	2.279	2.270	118.8	3.3	-21.8	-173.6
1W[bO^-]-[CO_2^-]-ctgg$_+$	2.219	2.202	124.0	-172.9	-169.3	-4.5
1W[CO_2^-]-ctgg$_-$	2.315, 2.359	2.272	89.1, 86.5	-178.3, 178.3	-169.0, 12.5	-177.6, 177.0
1W[HO]-[N,CO,S]-tggg$_+$	2.287	5.614	112.0	-17.6	-23.0	-114.9
1W[COOH]-ctgg$_+$	2.315	2.257	98.6	-177.0	-170.6	-173.7
1W[bO^-]-[CO_2^-]-cgtg	2.217	2.203	124.2	179.1	168.3	-1.0
TS-1W[CO_2^-/COOH]-ctgg$_+$	2.326	2.262	92.8	-176.8	-173.3	179.4
1W[bCO]-[CO_2^-]-ctgg$_+$	2.241	2.193	116.4	174.2	16.8	2.3
1W[bOH]-[CO]-ctgg$_-$	2.228	2.226	133.4	177.6	-170.7	2.7
1W[bOH]-[CO]-ctgg$_+$	2.232	2.226	132.9	-173.5	-173.1	-3.8
1W[HN]-[CO_2^-]-ctgg$_+$	2.282, 2.307	7.270	88.5, 86.9	-175.2, 175.3	-165.1, 16.8	13.0, -43.1
1W[bO^-]-[CO_2^-]-cggg	2.225	2.202	123.9	-175.1	-171.7	-2.5

Table 2. Continued.

Species[a]	r(Na^+-O=C) (Å)	r(Na^+-OH_2) (Å)	∠Na^+-O=C (°)	∠Na^+-O=C-C (°)	∠N-C-C=O (°)	∠C=O-Na^+-OH_2 Dihedral (°)
2W[N,CO,S]-tggg$_+$	2.391	2.307, 2.315	113.9	-16.3	-20.3	-109.1, 140.1
2W[N,CO,S]-tggg$_-$	2.341	2.302, 2.330	114.9	-16.8	-19.6	-120.1, 130.1
2W[HO]-[N,CO,S]-tggg$_+$	2.319	2.285, 5.649	112.6	-18.3	-21.6	178.2, -116.1
2W[bO$^-$]-[CO_2^-]-ctgg$_+$	2.253	2.230, 2.285	125.4	-173.1	-168.7	-3.8, 176.8
2W[N,CO]-tcgg	2.305	2.298, 2.309	120.2	4.8	12.3	-123.3, 105.3
2W[bOH]-[CO]-ctgg$_+$	2.268	2.252, 2.276	134.2	-174.1	-172.3	-3.4, 175.5
2W[bOH]-[CO]-ctgg$_-$	2.264	2.252, 2.276	134.6	178.4	-170.2	2.4, -179.0
2W[bO$^-$]-[CO_2^-]-cgtg	2.250	2.232, 2.286	125.5	179.0	168.4	-0.8, -180.0
2W[bO$^-$]-[CO_2^-]-ctgg$_-$	2.251	2.231, 2.286	125.3	-177.8	-169.2	0.5, -180.0
2W[bCO]-[CO_2^-]-ctgg$_+$	2.275	2.220, 2.287	119.2	174.7	16.2	1.7, 178.5
TS-2W[bO$^-$/bOH]-[CO_2^-/CO]-ctgg$_+$	2.262	2.244, 2.280	129.5	-175.0	-174.7	-4.1, 175.6
2W[HN]-[CO_2^-]-ctgg$_+$	2.310, 2.338	2.275, 7.293	88.7, 87.0	-175.1, 175.2	-165.0, 16.9	176.1, 13.2
2W[bOH]-[CO]-cgtg	2.265	2.254, 2.276	134.8	179.5	169.9	-0.8, -180.0
TS-2W[bO$^-$/bOH]-[CO_2^-/CO]-ctgg$_-$	2.260	2.244, 2.281	129.3	179.8	-174.1	0.7, 179.2
2W[bOH,bS]-[CO]-ctgt	2.251	2.253, 2.271	144.8	158.5	-169.8	-135.6, 19.5
2W[HN,bO$^-$]-[CO_2^-]-ctgg$_+$	2.211	2.200, 7.916	123.4	-173.3	-168.0	-4.1, 29.1
2W[HN]-[CO_2^-]-ctgg$_-$	2.304, 2.343	2.276, 7.242	88.9, 86.6	-178.6, 178.6	-168.5, 13.2	178.7, 14.8
2W[bO$^-$]-[CO_2^-]-cggg	2.257	2.231, 2.284	125.6	-175.5	-172.2	-2.7, 177.4
2W[HN,bO$^-$]-[CO_2^-]-ctgg$_-$	2.208	2.200, 7.900	123.5	-179.1	-168.9	0.8, 27.4
2W[bO$^-$,bS]-[CO_2^-]-cggt	2.252	2.245, 2.267	130.8	166.7	-175.7	11.9, -138.6
2W[HN]-[COOH]-ctgg$_+$	2.312, 2.455	2.260, 7.231	97.0, 87.4	-177.5, 178.0	-171.4, 10.2	179.8, 21.7
2W[HN,bO$^-$]-[CO_2^-]-cggg$_-$	2.216	2.199, 7.809	123.2	-176.2	-169.9	-2.0, 29.5
2W[HN,bOH]-[CO]-ctgg$_+$	2.225	2.224, 7.746	131.7	-175.2	-173.3	-2.8, 43.4

Table 2. Continued.

Species[a]	$r(Na^+\text{-}O{=}C)$ (Å)	$r(Na^+\text{-}OH_2)$ (Å)	$\angle Na^+\text{-}O{=}C$ (°)	$\angle Na^+\text{-}O{=}C\text{-}C$ (°)	∠N-C-C=O (°)	$\angle C{=}O\text{-}Na^+\text{-}OH_2$ Dihedral (°)
3W[bOH,bS]-[CO]-ctgt	2.311	2.296, 2.299, 2.300	135.5	146.7	-168.1	30.4, 150.1, -89.0
3W[HO,bCO]-[N,CO,S]-tggg$_+$	2.477	2.287, 2.314, 5.896	111.2	-22.7	-17.3	179.2, -94.7, -104.8
3W[bOH]-[CO]-ctgg$_+$	2.315	2.288, 2.305, 2.306	135.5	-176.8	-171.2	1.9, -105.7, 130.8
3W[HN,bO$^-$]-[CO_2^-]-ctgg$_+$	2.243	2.227, 2.288, 7.963	124.9	-173.8	-167.7	-3.2, 178.7, 29.8
3W[bO$^-$,bW]-[CO_2^-]-ctgg$_+$	2.282	2.285, 2.299, 2.381	127.0	-178.0	-168.1	-67.4, 142.6, 2.9
3W[bS,bCO,bW]-[N,CO]-tggg$_+$	2.429	2.271, 2.314, 2.384	119.3	-13.5	-5.7	-69.6, 104.0, 172.9
3W[bS,CO,bW]-[N,CO]-tggt	2.473	2.296, 2.303, 2.379	119.0	-10.5	-11.2	-60.5, 114.1, -176.7
3W[HO,bS]-[N,CO]-tggg$_+$	2.307	2.263, 2.302, 5.655	119.6	-13.3	-8.0	-71.0, 137.6, -141.1
3W[bOH]-[CO]-cgtg	2.310	2.289, 2.305, 2.307	136.3	178.0	169.3	3.3, -104.0, 131.6
3W[HN,bCO]-[CO_2^-]-ctgg$_+$	2.263	2.217, 2.290, 7.244	119.1	174.9	17.4	1.1, -179.9, -136.5
TS-3W[bOH/bO$^-$,bW]-[CO/CO_2^-]-ctgg$_+$	2.295	2.281, 2.298, 2.362	130.8	180.0	-174.1	-71.4, 140.6, 2.9
TS-3W[bOH/bO$^-$,bS/bW]-[CO/CO_2^-]-ctgt	2.302	2.284, 2.302, 2.316	128.2	151.6	-171.5	26.5, 148.5, -90.2
3W[bO$^-$,bW]-[CO_2^-]-cgtg	2.277	2.282, 2.300, 2.386	127.5	174.2	168.5	-65.2, 143.9, 4.7
3W[bOH]-[CO]-cgtt	2.310	2.290, 2.305, 2.307	136.3	-174.1	173.6	-6.5, 102.4, -135.1
3W[bOH,bW]-[CO]-ctgg$_-$	2.279	2.284, 2.300, 2.381	127.0	177.8	-169.2	-64.2, 145.5, 5.9
3W[bO$^-$,bW]-[CO_2^-]-ctgg$_-$	2.278	2.283, 2.300, 2.380	127.2	-174.1	-168.9	65.0, -143.7, -5.2
3W[HN,bCO]-[CO_2^-]-ctgg$_-$	2.263	2.217, 2.290, 7.190	118.2	178.5	12.9	-1.4, 177.7, -133.7
TS-3W[HN,bO$^-$/bOH]-[CO_2^-/CO]-ctgg$_+$	2.256	2.244, 2.280, 7.721	130.1	-175.8	-174.7	-3.2, 177.5, 38.6
3W[HN,bOH]-[CO]-ctgg$_+$	2.259	2.250, 2.277, 7.835	133.5	-175.1	-172.8	-3.0, 178.4, 44.7
3W[bO$^-$,bS]-[CO_2^-]-cggg	2.296	2.280, 2.302, 2.304	131.0	164.5	-179.1	9.5, -125.9, 124.3
3W[HNf,bO$^-$]-[CO_2^-]-cggg	2.247	2.228, 2.287, 7.849	124.9	-176.3	-170.4	-2.4, 177.1, 31.0
3W[HNr,bO$^-$]-[CO_2^-]-cggg	2.246	2.228, 2.287, 7.251	125.1	-173.7	-170.3	-3.8, 174.1, -46.3
3W[bO$^-$,bW]-[CO_2^-]-cggg	2.287	2.282, 2.300, 2.369	127.2	-171.5	-172.3	-8.0, -147.3, 63.6

Table 2. Continued.

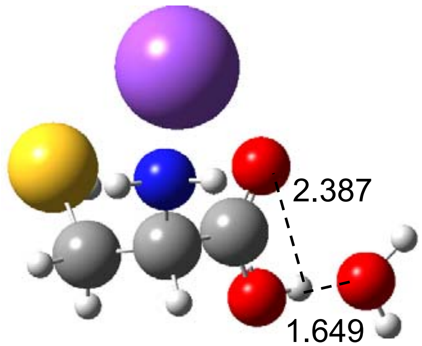
Species[a]	r(Na$^+$-O=C) (Å)	r(Na$^+$-OH$_2$) (Å)	∠Na$^+$-O=C (°)	∠Na$^+$-O=C-C (°)	∠N-C-C=O (°)	∠C=O-Na$^+$-OH$_2$ Dihedral (°)
4W[HN,bO$^-$,bW]-[CO$_2^-$]-ctgg$_+$	2.269	2.285, 2.301, 2.384, 8.056	126.9	-178.4	-167.1	-66.8, 2.6, 143.2, 27.2
4W[bOH,AA]-[CO]-ctgg$_+$	2.324	2.290, 2.296, 2.297, 4.085	137.2	-174.4	-171.5	-6.6, -134.6, 117.4, 171.3
4W[HN-bW,bO$^-$,AD]-[CO$_2^-$]-cgtg$_-$	2.236	2.292, 2.373, 2.548, 4.528	120.0	-148.0	149.8	-172.3, -22.1, 44.3, 50.4
4W[HO,bS,bCO,bW]-[N,CO]-tggg$_+$	2.416	2.273, 2.303, 2.425, 5.866	120.0	-14.0	-6.7	-66.6, 113.3, 177.7, -145.4
4W[HN,bO$^-$,bW]-[CO$_2^-$]-cgtg$_-$	2.265	2.288, 2.301, 2.388, 7.070	127.1	171.7	169.5	-62.1, 149.0, 6.8, 53.6
4W[HN-bO$^-$r,bO$^-$,bWr]-[CO$_2^-$]-cgtg$_-$	2.267	2.284, 2.301, 2.387, 5.913	129.0	-179.1	174.5	-61.4, 146.5, 6.6, -28.0
4W[HN-bO$^-$f,bO$^-$,bWf]-[CO$_2^-$]-cgtg$_-$	2.266	2.284, 2.301, 2.391, 5.845	128.7	-177.8	-177.2	59.8, -147.9, -8.1, 31.7
4W[bOH,AA]-[CO]-cgtg$_-$	2.323	2.291, 2.296, 2.296, 4.084	138.0	179.5	168.7	-1.5, 124.0, -128.2, 177.8
4W[HN,bO$^-$,bW]-[CO$_2^-$]-ctgg$_-$	2.267	2.286, 2.300, 2.387, 8.024	126.9	177.4	-168.5	-62.4, 147.3, 6.5, 27.0
4W[bO$^-$,AA]-[CO$_2^-$]-ctgg$_+$	2.305	2.272, 2.308, 2.313, 4.125	128.6	-173.9	-167.7	-2.5, 126.1, -125.8, 179.4
4W[bS,bCO,bHN,bW]-[N,CO]-tggg$_+$	2.627	2.307, 2.380, 2.421, 2.449	117.8	-16.3	-0.1	-58.8, -79.2, 94.8, 164.4
4W[HN-bW,bO$^-$,AD]-[CO$_2^-$]-cgtg$_+$	2.236	2.292. 2.375, 2.544, 4.530	120.3	-147.1	150.3	-172.7, -22.6, 43.8, 50.0
4W[HN-bS,bO$^-$,bW]-[CO$_2^-$]-cgtg$_-$	2.269	2.285, 2.301, 2.386, 7.498	127.0	-172.2	-174.9	62.3, -148.1, -7.1, -45.3
4W[bS,bOH,AD]-[CO]-ctgt	2.314	2.237, 2.298, 2.442, 3.521	137.2	146.8	-168.8	130.8, -83.8, 31.4, 83.5
4W[HO,bS,bW]-[N,CO]-tggt	2.363	2.297, 2.344, 2.454, 5.714	120.3	-15.0	-10.2	-131.8, 112.0, -46.8, -142.9
TS-4W[bOH/bO$^-$,AA]-[CO/CO$_2^-$]-ctgg$_+$	2.315	2.282, 2.303, 2.304, 4.105	131.9	-175.3	-174.0	-4.1, 121.3, -131.0, 175.2
4W[HN,bO$^-$,bW]-[CO$_2^-$]-cgtt	2.265	2.287, 2.301, 2.389, 7.164	127.4	173.6	171.0	-62.8, 148.0, 5.9, 52.9
4W[AA-bCO]-[CO$_2^-$]-ctgg$_+$	2.307	2.295, 2.296, 2.319, 3.431	127.0	176.5	13.6	48.1, 49.7, -173.6, 0.3
4W[HO-bCO,bW,AD]-[N,CO]-tggg$_+$	2.334	2.258, 2.304, 4.212, 4.819	116.0	22.2	6.2	95.9, -137.9, 93.0, 125.7
4W[HN-bO$^-$,bO$^-$,bW]-[CO$_2^-$]-cgtg$_+$	2.265	2.283, 2.301, 2.394, 5.833	128.9	-176.8	-177.8	58.8, -149.6, -8.9, 32.0
4W[AA-bO$^-$]-[CO$_2^-$]-cgtg$_-$	2.279	2.292, 2.295, 2.314, 3.460	137.3	179.9	167.6	-49.9, 45.2, 177.6, -2.2
4W[HN-bS,bO$^-$,bW]-[CO$_2^-$]-cgtt	2.271	2.287, 2.300, 2.387, 7.683	126.7	-171.2	-177.8	60.2, -150.3, -9.2, -41.5
4W[bOH,AD-CO]-[CO]-ctgt	2.423	2.249, 2.284, 2.302, 3.689	131.7	-164.6	-167.1	-151.2, -14.9, 94.4, -153.8

Table 2. Continued.

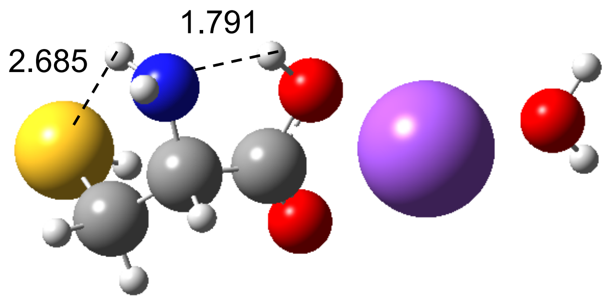
Species[a]	$r(Na^+\text{-}O{=}C)$ (Å)	$r(Na^+\text{-}OH_2)$ (Å)	∠Na$^+$-O=C (°)	∠Na$^+$-O=C-C (°)	∠N-C-C=O (°)	∠C=O-Na$^+$-OH_2 Dihedral (°)
4W[bO$^-$,AA]-[CO_2^-]-cgtg$_-$	2.303	2.273, 2.309, 2.312, 4.126	128.7	179.3	168.6	-2.1, 122.5, -129.0, 176.4
4W[bOH,AA]-[CO]-cgtt	2.321	2.292, 2.296, 2.296, 4.085	138.1	-176.8	173.0	-3.8, -130.7, 121.3, 174.8
4W[AA-bN]-[CO]-tggg	2.302	2.271, 2.293, 2.414, 3.720	134.3	-126.9	113.7	71.4, -143.5, -16.5, 33.0
TS-4W[HN,bO$^-$/bOH, bW]-[CO_2^-/CO]-ctgg$_+$	2.288	2.282, 2.297, 2.367, 7.834	131.5	178.7	-174.2	-70.0, 142.5, 3.8, 37.6
4W[HN,bOH]-[CO]-ctgg$_+$	2.305	2.285, 2.306, 2.307, 7.960	134.9	-178.0	-172.0	1.8, -106.5, 131.5, 45.2
4W[bO$^-$,bW,AD]-[CO_2^-]-cgtg$_-$	2.276	2.276, 2.353, 2.402, 3.547	127.8	-174.5	-169.6	-140.9, 99.6, -3.2, 45.3
4W[AA-bCO]-[CO_2^-]-ctgg$_-$	2.309	2.288, 2.296, 2.319, 3.431	126.2	178.0	12.0	49.2, -48.6, -173.3, 0.0
4W[bO$^-$,AD-CO]-[CO_2^-]-ctgt	2.391	2.262, 2.279, 2.305, 3.653	125.1	-162.6	-166.7	-160.2, -15.8, 82.3, -157.3

[a] Names and numbers in bold indicate the lowest energy structures for complexes.

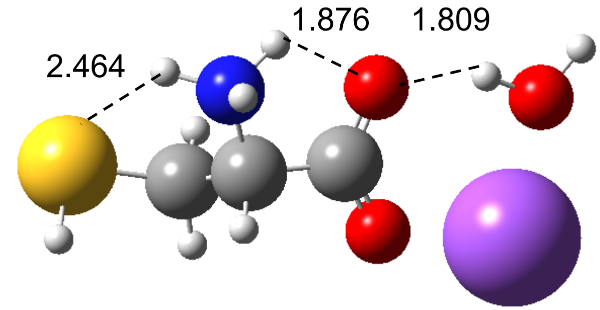
[b] All geometric parameters refer to Na-O(H) instead of Na-OC.



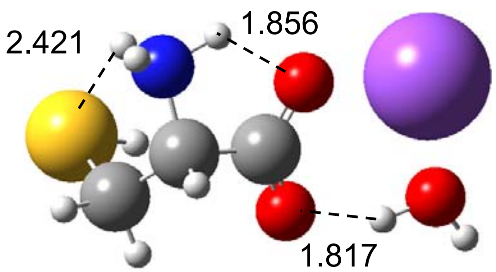
1W[HO]-[N,CO,S]-tggg$_{+}$, 13-19



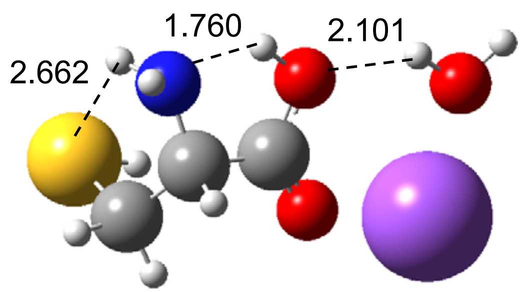
1W[COOH]-ctgg$_{+}$, 14-22



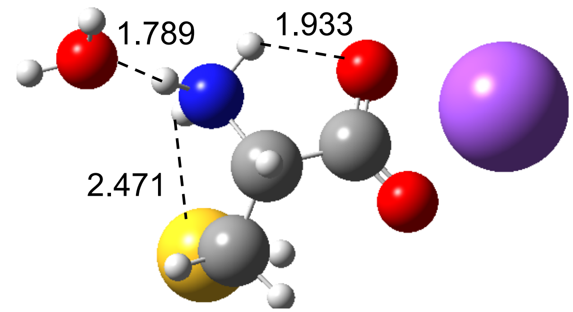
1W[bO^{-}]-[CO_2^{-}]-cgtg, 14-23



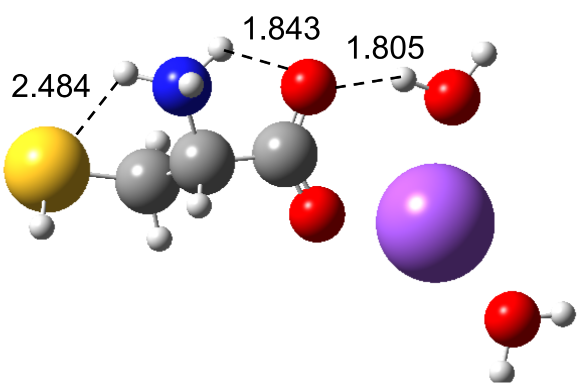
1W[bCO]-[CO_2^{-}]-ctgg$_{+}$, 15-23



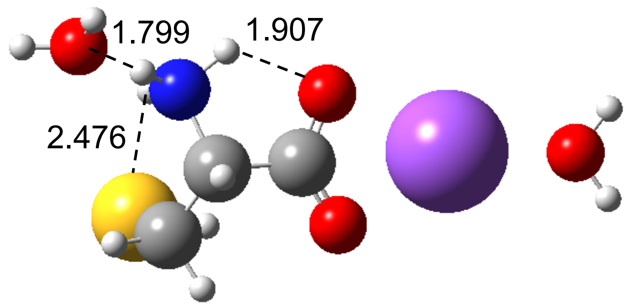
1W[bOH]-[CO]-ctgg$_{+}$, 17-26



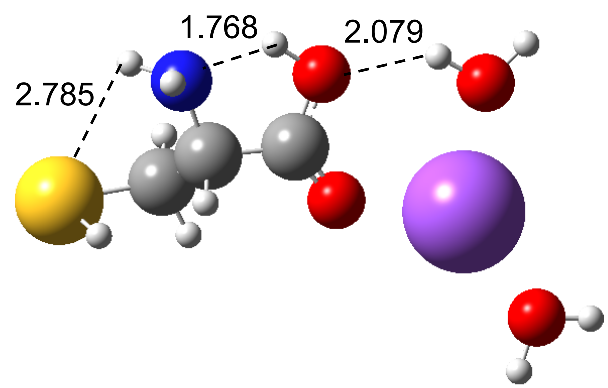
1W[HN]-[CO_2^{-}]-ctgg$_{+}$, 22-29



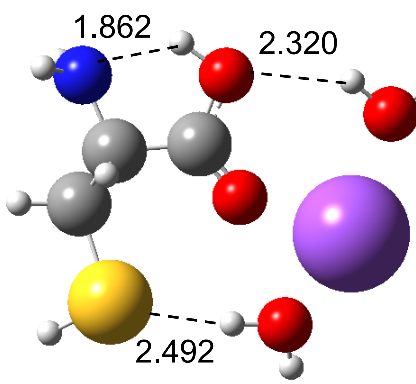
2W[bO^{-}]-[CO_2^{-}]-cgtg, 3-14



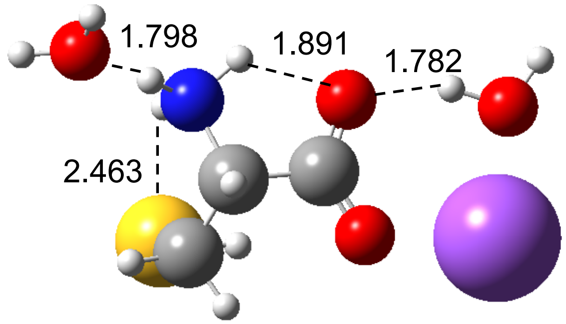
2W[HN]-[CO_2^{-}]-ctgg$_{+}$, 8-15



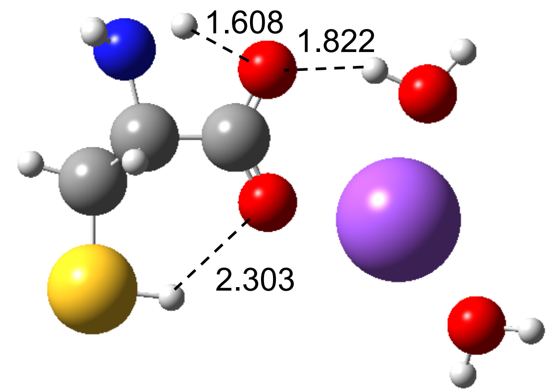
2W[bOH]-[CO]-cgtg, 5-16



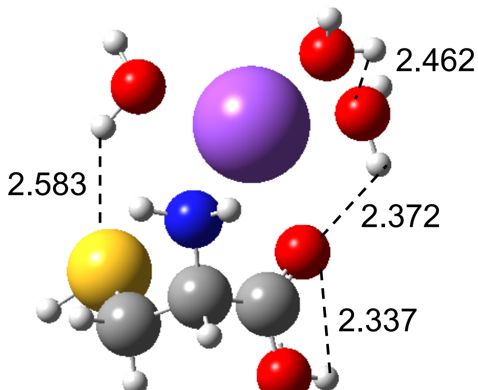
2W[bOH,bS]-[CO]-ctgt, 14-20



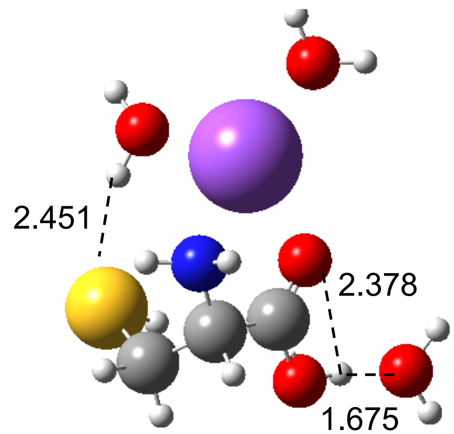
2W[HN,bO$^-$]-[CO$_2^-$]-ctgg$_+$, 12-21



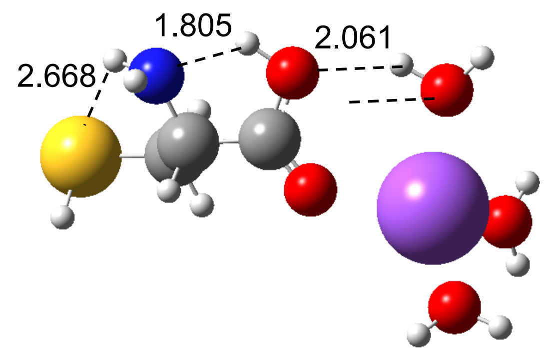
2W[bO$^-$]-[CO$_2^-$]-cggg, 24-34



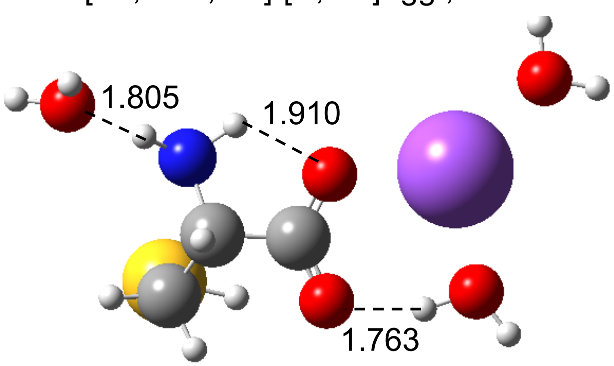
3W[bS,bCO,bW]-[N,CO]-tggt, 8-22



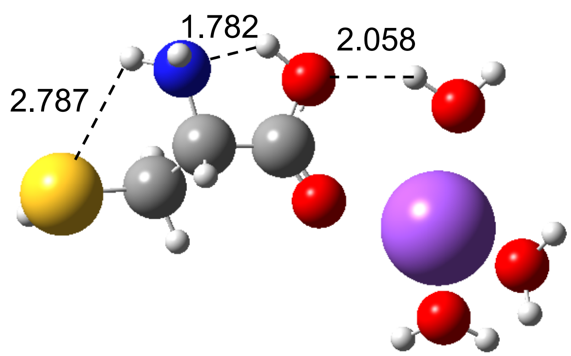
3W[HO,bS]-[N,CO]-tggg$_+$, 7-10



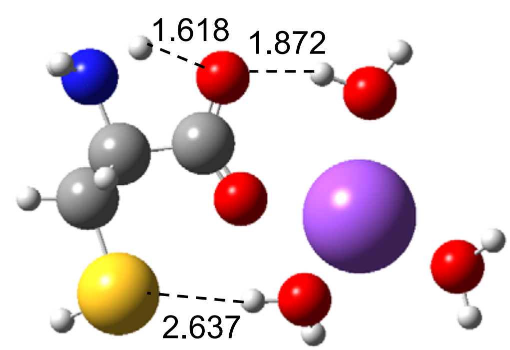
3W[bOH]-[CO]-cgtg, 4-10



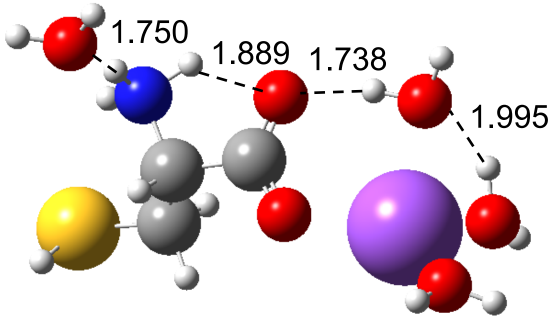
3W[HN,bCO]-[CO$_2^-$]-ctgg$_+$, 6-11



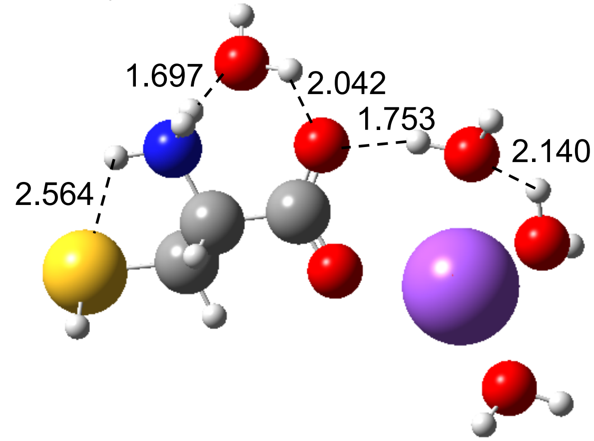
3W[bOH]-[CO]-cgtt, 8-14



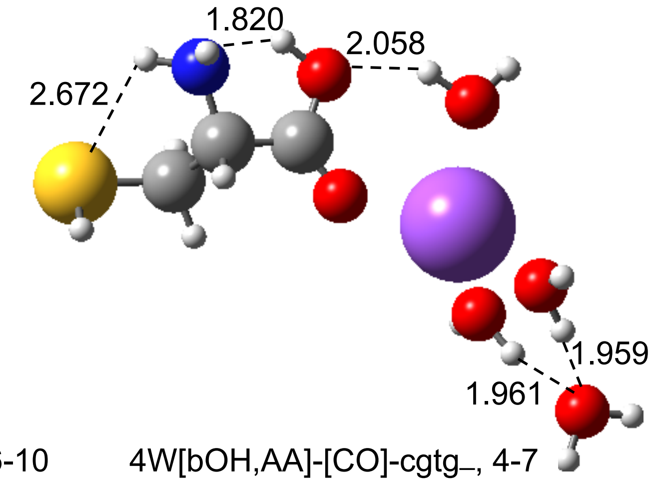
3W[bO$^-$,bS]-[CO$_2^-$]-cggg, 28-29



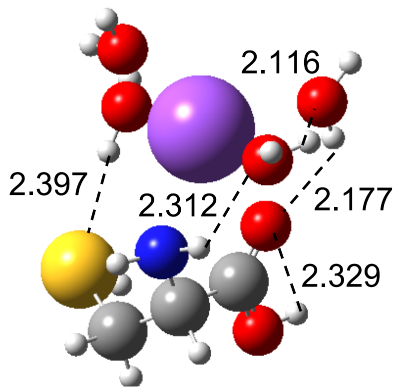
4W[HN,bO$^-$,bW]-[CO$_2^-$]-cgtg$_-$, 4-6



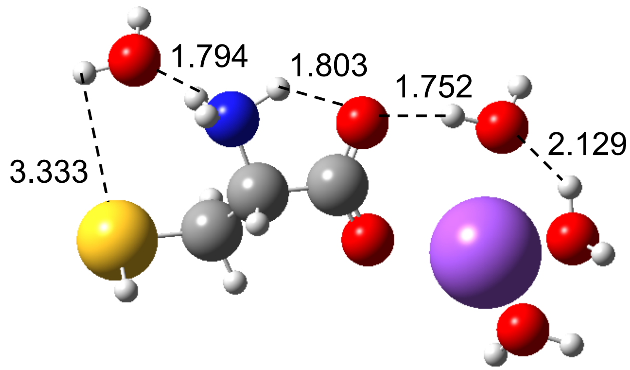
4W[HN-bO$^-$r,bO$^-$,bWr]-[CO$_2^-$]-cgtg$_-$, 6-10



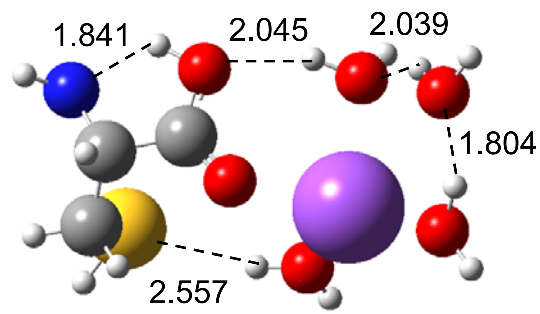
4W[bOH,AA]-[CO]-cgtg$_-$, 4-7



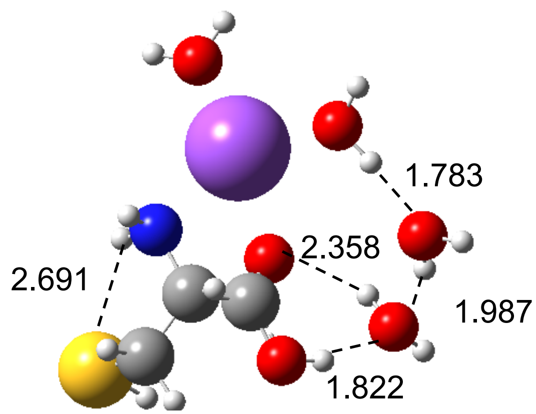
4W[bS,bCO,bHN,bW]-[N,CO]-tggg$_+$, 8-28



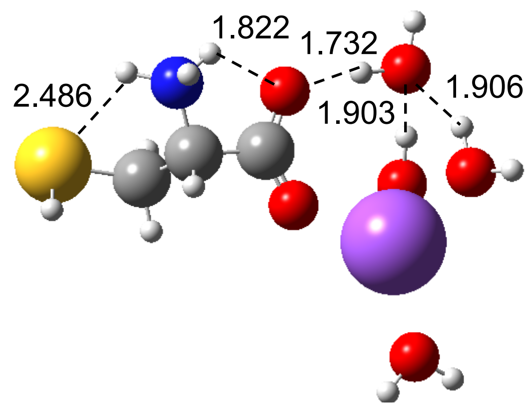
4W[HN-bS,bO$^-$,bW]-[CO$_2^-$]-cgtg$_-$, 9-11



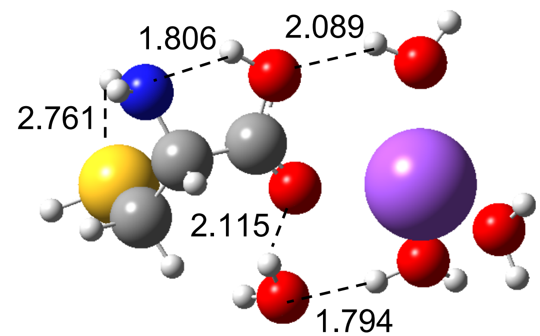
4W[bS,bOH,AD]-[CO]-ctgt, 9-14



4W[HO-bCO,bW,AD]-[N,CO]-tggg$_+$, 10-18



4W[AA-bO$^-$]-[CO$_2^-$]-cgtg$_-$, 10-12



4W[bOH,AD-CO]-[CO]-ctgt, 13-19