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Supplementary Information for:

"Structural Characterization of Gas-Phase Cysteine and Cysteine Methyl Ester Complexes with Zinc and Cadmium Dications by Infrared Multiple Photon Dissociation Spectroscopy"

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Table S1. Relative enthalpy at 0 K (ΔH_0) and free energies (ΔG_{298}) [a] (kJ/mol) at 298 K of metal cationized (Cys-H), (CysOMe-H), and CysOMe Conformers [b]

Complex	Structure	B3LYP		B3P86		MP2(full)	
$[Zn(Cys-H)]^+$	[N,CO,S$^-$]tgg	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
	[N,CO,S$^-$]cgg	24.1	(26.6)	23.6	(26.2)	22.9	(25.4)
	[CO,S$^-$]cgg	30.0	(31.4)	33.7	(35.1)	47.2	(48.7)
	[N,S$^-$]tgt	33.8	(37.1)	40.6	(44.0)	41.0	(44.3)
	[CO$^-$,S$^-$]cgg[c]	39.4	(40.0)	43.9	(44.5)	45.4	(46.0)
	[N,OH,S$^-$]tgg	40.8	(41.4)	44.8	(45.4)	37.8	(38.4)
	[CO,S$^-$]ctg	53.0	(53.6)	57.3	(58.0)	71.2	(71.8)
	[N,CO$^-$,S]ggg$_+$	61.4	(62.1)	61.6	(62.3)	58.9	(59.6)
	[N,S$^-$]cgt	66.7	(70.3)	73.1	(76.6)	74.4	(78.0)
	[N,CO$^-$,S]ggg$_-$	67.1	(67.4)	68.1	(68.3)	66.2	(66.5)
	[N$^-$,CO,S]cggg$_+$	99.3	(102.2)	100.4	(103.3)	101.3	(104.2)
	[N$^-$,CO,S]tggg	100.6	(103.6)	101.6	(104.6)	102.9	(105.9)
	[N$^-$,CO,S]cggg$_-$	121.4	(124.4)	121.6	(124.7)	122.8	(125.9)
	[CO_2^-,S]gcg	140.5	(142.7)	144.6	(146.8)	155.7	(158.0)
	[N,CO$^-$]cgg	141.4	(142.3)	150.0	(150.9)	145.0	(145.9)
	[N,CO$^-$]gtg	145.1	(146.3)	154.6	(155.8)	152.6	(153.8)
	[N,CO$^-$]tg$_-$g	147.4	(148.8)	156.3	(157.7)	153.0	(154.4)
	[S$^-$]tgg	150.6	(155.3)	171.1	(175.8)	186.7	(191.4)
	[N,CO$^-$]gtt	151.4	(153.0)	161.2	(162.8)	159.3	(160.9)
	[CO$^-$,S]ggg	157.7	(160.8)	168.5	(171.6)	178.6	(181.7)
	[S$^-$]ttc	163.6	(169.4)	185.8	(191.7)	217.0	(222.8)
	[N,CO$^-$]tg$_+$g	166.4	(170.4)	179.4	(183.3)	176.7	(180.6)
	[N$^-$,CO]tcgg	170.7	(175.4)	182.2	(186.9)	182.6	(187.3)
	[CO_2^-]gtg$_+$	177.1	(181.2)	199.5	(203.5)	249.8	(253.8)
	[CO_2^-]ggg	179.7	(184.5)	201.4	(206.2)	241.0	(245.8)
	[N$^-$,CO]cctt	181.6	(186.3)	191.4	(196.1)	190.0	(194.7)
	[CO_2^-]gtg$_-$	181.8	(187.2)	204.6	(210.0)	255.0	(260.4)

Complex	Structure	B3LYP		B3P86		MP2(full)	
$[Zn(Cys\text{-}H)]^+$	$[N^-,S]cttg$	191.5	(196.6)	200.6	(205.8)	203.0	(208.1)
	[N,CO,CH]tgt	239.8	(242.9)	251.5	(254.7)	303.9	(307.0)
	[N,CO]tgt	241.0	(242.2)	258.1	(259.3)	343.4	(344.5)
	[N,CO]tgg	242.1	(243.1)	259.5	(260.4)	344.9	(345.9)
	$[CO_2^-]gt^c$	271.1	(249.1)	291.7	(269.7)	396.0	(374.0)
$[Cd(Cys\text{-}H)]^+$	$[N,CO,S^-]tgg$	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
	$[N,CO,S^-]cgg$	25.1	(25.3)	24.6	(24.8)	25.9	(26.0)
	$[N,S^-]tgt$	26.0	(26.6)	31.0	(31.6)	35.9	(36.5)
	$[CO,S^-]cgg$	29.4	(30.0)	31.5	(32.0)	45.7	(46.3)
	$[N,OH,S^-]tgg$	34.0	(34.6)	38.3	(38.9)	34.4	(34.9)
	$[CO,S^-]ctg$	42.8	(43.0)	45.5	(45.8)	59.2	(59.4)
	$[CO^-,S^-]cgg^c$	45.6	(45.6)	46.9	(47.0)	50.7	(50.7)
	$[N,S^-]cgt$	58.4	(59.2)	62.6	(63.4)	68.2	(69.0)
	$[N,CO^-,S]ggg_+$	81.8	(81.6)	82.1	(81.9)	84.0	(83.8)
	$[S^-]tgg$	83.9	(85.3)	98.4	(99.8)	105.5	(106.9)
	$[N,CO^-,S]ggg_-$	87.9	(88.0)	88.8	(88.9)	91.8	(91.9)
	$[S^-]ttc$	99.8	(102.3)	115.8	(118.3)	144.5	(146.9)
	$[N^-,CO,S]tggg$	105.3	(105.8)	107.4	(107.9)	113.4	(113.9)
	$[CO_2^-,S]gcc$	121.0	(122.3)	125.4	(126.8)	146.0	(147.4)
	$[N^-,CO,S]cggg$	128.2	(128.8)	129.4	(130.0)	135.3	(135.9)
	$[CO_2^-]g_+tg$	129.9	(133.8)	151.5	(155.4)	227.9	(231.8)
	$[CO_2^-]cgg$	130.8	(134.4)	150.9	(154.4)	224.6	(228.2)
	$[CO_2^-]gg_-g$	132.1	(135.7)	152.1	(155.8)	224.2	(227.8)
	$[CO_2^-]gtg$	132.9	(137.9)	155.7	(160.7)	232.4	(237.3)
	$[CO_2^-]gg_+g$	140.0	(143.9)	160.8	(164.8)	236.9	(240.8)
	$[N,CO^-]tgg_+$	149.4	(149.9)	156.7	(157.1)	163.0	(163.5)
	$[N,CO^-]tgg_-$	155.9	(156.9)	163.4	(164.4)	171.5	(172.5)
	$[N,CO^-]gtt$	156.6	(158.0)	164.8	(166.2)	174.8	(176.2)

Complex	Structure	B3LYP		B3P86		MP2(full)	
$[Cd(Cys-H)]^+$	$[CO^-,S]$ggt	160.2	(162.6)	167.8	(170.2)	187.9	(190.2)
	$[CO_2^-,S]$ggg	164.2	(166.4)	171.8	(174.0)	193.3	(195.5)
	$[N^-,CO]$tcgg	166.4	(168.2)	179.8	(181.6)	198.8	(200.6)
	$[N,CO_2^-]$tgg	166.5	(167.5)	178.6	(179.6)	197.0	(198.0)
	$[N^-,CO]$cctt	181.4	(184.2)	191.2	(194.0)	200.5	(203.3)
	$[N^-,S]$cttg	184.6	(186.8)	193.1	(195.2)	207.8	(209.9)
	[N,CO,CH]tgt	199.8	(200.4)	214.3	(214.9)	259.3	(259.9)
	$[CO_2^-]$ggt[c]	200.1	(201.8)	218.5	(220.2)	302.5	(304.1)
	[N,CO]tgg	204.1	(204.9)	221.6	(222.4)	289.9	(290.7)
	[N,CO]tcg	235.9	(238.3)	261.2	(263.6)	164.4	(166.8)
	[CO,S]ttgt	285.4	(287.2)	300.9	(302.7)	385.2	(387.0)
$[Zn(CysOMe-H)]^+$	$[N,CO,S^-]$tgg	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
	$[N,CO,S^-]$cgg	35.8	(35.9)	34.8	(34.8)	35.8	(35.8)
	$[N,S^-]$tgt	40.3	(41.2)	46.7	(47.6)	49.9	(50.8)
	$[N,OMe,S^-]$tgg	44.4	(44.8)	46.9	(47.4)	37.9	(38.3)
	$[CO,S^-]$tgg	58.9	(60.7)	67.3	(69.2)	77.5	(79.3)
	$[CO,S^-]$ct_g	78.4	(79.7)	85.0	(86.2)	95.0	(96.3)
	$[N,S^-]$cgt	86.7	(87.4)	91.9	(92.6)	95.2	(95.9)
	$[CO,S^-]$ct$_+$g	87.7	(89.1)	95.2	(96.5)	106.5	(107.8)
	$[N^-,CO,S]$tggg	102.7	(103.2)	103.6	(104.2)	106.2	(106.8)
	$[N^-,OMe,S]$tggg	153.1	(154.2)	157.2	(158.3)	151.8	(152.9)
	[N,CO]tgt	240.8	(242.1)	257.8	(259.0)	340.4	(341.7)
	[N,CO]tcg	241.3	(242.1)	258.3	(259.2)	338.8	(339.7)
$[Cd(CysOMe-H)]^+$	$[N,CO,S^-]$tgg	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
	$[N,S^-]$tgt	30.0	(30.6)	34.5	(35.1)	40.2	(40.9)
	$[N,CO,S^-]$cgg	37.4	(37.5)	36.3	(36.4)	37.8	(37.9)
	$[N,OMe,S^-]$tgg	38.4	(38.8)	41.3	(41.6)	35.0	(35.3)
	$[CO,S^-]$tgg	53.9	(55.4)	60.5	(62.0)	73.2	(74.7)

Complex	Structure	B3LYP		B3P86		MP2(full)	
$[Cd(CysOMe-H)]^+$	$[CO,S^-]ct_-g$	74.0	(75.1)	78.7	(79.8)	92.2	(93.3)
	$[N,S^-]cgt$	75.2	(75.6)	78.3	(78.7)	84.1	(84.6)
	$[CO,S^-]ct_+g$	78.9	(80.2)	84.9	(86.2)	100.3	(101.5)
	$[N^-,CO,S]tggg$	104.6	(105.0)	106.7	(107.1)	112.9	(113.3)
	$[N^-,OMe,S]tggg$	145.8	(146.9)	151.4	(152.5)	153.6	(154.8)
	[N,CO]tgt	201.5	(202.6)	218.3	(219.4)	289.7	(290.8)
	[N,CO] tgg	203.7	(204.4)	220.8	(221.5)	291.0	(291.7)
$CdCl^+$(CysOMe)	$[N,CO,S]tggg_+$	0.0	(0.0)	0.0	(0.0)	0.0	(0.0)
	$[N,CO,S]tggg_-$	1.7	(2.0)	1.8	(2.1)	2.3	(2.6)
	$[S^-]tcg^c$	20.7	(20.8)	21.3	(21.4)	24.7	(24.8)
	$[N,CO]tgtg_-$	22.3	(22.6)	27.1	(27.4)	33.3	(33.6)
	[N,CO]tggg	22.9	(23.0)	27.4	(27.6)	32.8	(33.0)
	[N,CO]tcgg	24.9	(25.7)	29.6	(30.4)	35.5	(36.3)
	[N,S]tgtg	27.2	(27.8)	29.8	(30.3)	37.5	(38.0)
	$[N,CO]tgtg_+$	27.1	(28.2)	32.0	(33.1)	38.7	(39.7)
	$[CO,S]ttg^c$	28.5	(28.5)	29.2	(29.2)	33.5	(33.4)
	$[N,OMe,S]tggg_+$	29.5	(29.7)	30.4	(30.7)	23.2	(23.5)
	$[N,OMe,S]tggg_-$	33.7	(34.1)	35.0	(35.4)	28.2	(28.6)
	[N,CO,S]cggg	40.6	(40.6)	39.8	(39.7)	41.1	(41.0)
	[CO,S]ttgt	56.5	(58.3)	62.3	(64.2)	78.1	(80.0)
	$[CO,S]cgg^c$	69.3	(69.7)	67.8	(68.2)	75.3	(75.7)
	[CO,S]ctgt	86.2	(87.6)	91.2	(92.7)	107.9	(109.3)
	[CO,S]ctgg	89.8	(91.1)	94.6	(95.9)	112.0	(113.3)
	[CO]cggg	126.5	(128.2)	136.9	(138.7)	153.2	(155.0)
	$[CO,OMe]ggc^c$	169.3	(168.3)	158.8	(157.9)	153.9	(152.9)
	$[CO]tgc^c$	175.4	(174.9)	166.1	(165.6)	164.6	(164.1)

[a] Free energies at 298 K given in parentheses. [b] Values are single point energies calculated at the stated level of theory using a 6-311+G(2d,2p) basis set for Zn containing complexes and def2TZVVP for Cd containing complexes. Geometries and vibrational frequencies calculated at B3LYP/6-311+G(d,p) level for Zn containing complexes and B3LYP/def2TZVP for Cd containing complexes. Energies include ZPE corrections scaled by 0.989. [c] Salt-bridge between NH_3^+, CO_2^-, and S^- groups.