Supporting Information

For

Synthetic Analogues of the Active Site of the A-cluster of Acetyl Coenzyme A Synthase/CO Dehydrogenase: Syntheses, Structures, and Reactions with CO

Todd C. Harrop,[a] Marilyn M. Olmstead,[b] and Pradip K. Mascharak[*a]

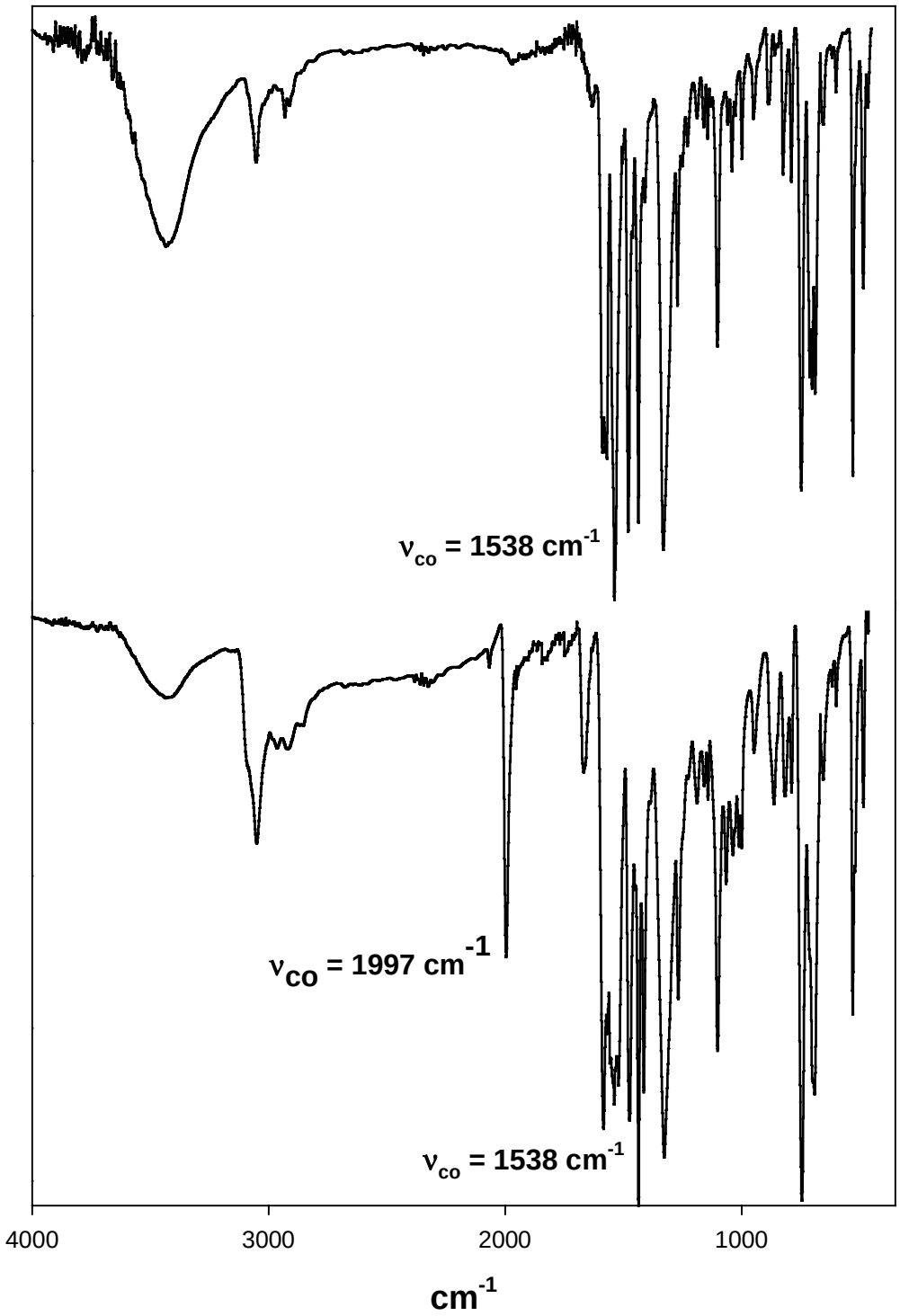

Figure S1. FTIR spectrum of [Ni(dppe)Ni(PhPepS)] (**10**, top panel) and [Ni^{I}(dppe)(CO)Ni(PhPepS)]$^{-}$ (**10$_{red}$-CO**, bottom panel) in KBr matrix.

Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for $(Et_4N)_2$[Ni(PhPepS)] (**2**), (Et_4N)[Cu(neo)Ni(NpPepS)]•0.5Et_2O•0.5H_2O (**3**•0.5Et_2O•0.5H_2O), (Et_4N)[Cu(neo)Ni(PhPepS)]•H_2O (**4**•H_2O), $(Et_4N)_2$[Ni{Ni(NpPepS)}$_2$]•DMF (**5**•DMF), $(Et_4N)_2$[Ni(DMF)$_2${Ni(NpPepS)}$_2$]•3DMF (**6**•3DMF), $(Et_4N)_2$[Ni(DMF)$_2${Ni(PhPepS)}$_2$] (**8**), [Ni(dppe)Ni(PhPepS)]•CH_2Cl_2 (**10**•CH_2Cl_2)

Parameters	**2**	**3**•0.5Et_2O•0.5H_2O	**4**•H_2O	**5**•DMF	**6**•3DMF	**8**	**10**•CH_2Cl_2
formula	$C_{36}H_{52}N_4O_2S_2Ni$	$C_{49}H_{49.5}N_5O_3S_2CuNi$	$C_{42}H_{46}N_5O_3S_2CuNi$	$C_{67}H_{74}N_7O_5S_4Ni_3$	$C_{79}H_{103}N_{11}O_9S_4Ni_3$	$C_{62}H_{78}N_8O_6S_4Ni_3$	$C_{47}H_{38}N_2O_2P_2S_2Cl_2Ni_2$
mol wt	695.65	930.80	855.21	1361.70	1655.09	1335.69	977.17
cryst color, habit	red needle	red plate	red needle	black block	red parallelepiped	red block	black prism
T, K	90(2)	93(2)	90(2)	90(2)	130(2)	90(2)	90(2)
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	12.6126(9)	12.4276(18)	19.9276(7)	18.6353(15)	17.009(3)	12.2141(15)	14.0656(5)
b, Å	19.7239(14)	17.482(2)	20.5446(7)	20.2119(17)	13.0882(16)	15.5332(17)	17.3249(6)
c, Å	14.6251(10)	22.792(3)	9.3913(3)	17.3241(14)	37.076(4)	16.2978(19)	17.5370(6)
α, deg	90	108.535(4)	90	90	90	90	90
β, deg	106.900(10)	93.198(6)	90	110.887(3)	101.902(12)	97.638(3)	90.610(3)
γ, deg	90	110.092(6)	90	90	90	90	90
V, $Å^3$	3421.0(4)	4332.9(10)	3844.8(2)	2816.1(13)	8076.0(2)	3064.7(6)	4273.3(3)
Z	4	4	4	4	4	2	4
d_{calcd}, $g{\cdot}cm^{-3}$	1.351	1.429	1.477	1.484	1.361	1.447	1.519
Abs coeff, μ, mm^{-1}	0.728	1.070	1.199	1.112	2.277	1.106	1.221
GOF[a] on F^2	1.010	1.008	1.086	1.052	1.004	1.089	1.001
R1,[b] %	4.49	5.64	2.80	4.99	4.60	6.44	3.12
wR2,[c] %	10.29	12.19	6.75	12.15	10.13	13.03	7.23

[a] GOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/M - N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R1 = \Sigma\big|\,|F_o| - |F_c|\,\big| / \Sigma|F_o|$; [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected Bond Distances [Å] and Bond Angles [deg] for the Complexes.

Complex **2**		Complex **3**				Complex **4**			
Ni-N1	1.908(3)	Ni1-Cu1	3.074(4)	N3-Cu1-S2	122.17(14)	Ni1-Cu1	3.1435(2)	N3-Cu1-S2	117.85(4)
Ni-N2	1.906(3)	Ni1-N1	1.889(5)	N4-Cu1-S2	115.89(14)	Ni1-N1	1.9115(13)	N4-Cu1-S2	113.79(4)
Ni-S1	2.1647(10)	Ni1-N2	1.908(4)	S1-Cu1-S2	87.46(6)	Ni1-N2	1.8958(11)	S1-Cu1-S2	83.869(14)
Ni-S2	2.1518(10)	Ni1-S1	2.1875(15)	O1-C7-N1	124.5(5)	Ni1-S1	2.1889(4)	O1-C7-N1	125.61(16)
C7-O1	1.249(4)	Ni1-S2	2.2025(16)	O1-C7-C6	117.0(5)	Ni1-S2	2.1855(4)	O1-C7-C6	117.64(15)
C7-N1	1.368(4)	Cu1-N3	2.037(5)	N1-C7-C6	118.4(5)	Cu1-N3	2.0194(14)	N1-C7-C6	116.56(14)
N2-Ni-N1	85.52(11)	Cu1-N4	2.057(4)	C1-S1-Ni1	101.19(18)	Cu1-N4	2.0894(14)	C1-S1-Ni1	99.06(5)
N2-Ni-S2	95.65(8)	Cu1-S1	2.2669(16)			Cu1-S1	2.2496(4)		
N1-Ni-S2	178.83(8)	Cu1-S2	2.3198(16)			Cu1-S2	2.3508(4)		
N2-Ni-S1	174.80(9)	C7-O1	1.252(7)			C7-O1	1.251(2)		
N1-Ni-S1	94.62(8)	C7-N1	1.345(7)			C7-N1	1.348(2)		
S2-Ni-S1	84.21(4)	N1-Ni1-N2	88.75(19)			N2-Ni1-N1	84.39(5)		
C1-S1-Ni	106.53(11)	N1-Ni1-S1	89.27(14)			N2-Ni1-S2	92.53(4)		
O1-C7-N1	123.9(3)	N2-Ni1-S1	177.81(15)			N1-Ni1-S2	168.98(5)		
O1-C7-C6	116.2(3)	N1-Ni1-S2	178.18(14)			N2-Ni1-S1	178.12(4)		
N1-C7-C6	119.8(3)	N2-Ni1-S2	89.50(14)			N1-Ni1-S1	93.73(4)		
		S1-Ni1-S2	92.49(6)			S2-Ni1-S1	89.335(15)		
		N3-Cu1-N4	82.66(18)			N3-Cu1-N4	82.08(5)		
		N3-Cu1-S1	129.80(14)			N3-Cu1-S1	140.13(4)		
		N4-Cu1-S1	122.59(14)			N4-Cu1-S1	121.41(4)		

Table 2 (continued). Selected Bond Distances [Å] and Bond Angles [deg] for the Complexes.

Complex **5**				Complex **6**			
Ni1-Ni2	3.2410(7)	S1-Ni2-S2	84.52(4)	Ni1-Ni2	3.374(4)	O5-Ni2-O6	85.60(12)
Ni2-Ni3	3.2128(7)	S3-Ni2-S4	84.67(4)	Ni2-Ni3	3.375(4)	O5-Ni2-S2	99.55(9)
Ni1-N1	1.884(3)	S1-Ni2-S4	177.97(4)	Ni1-N1	1.898(3)	O6-Ni2-S2	91.27(8)
Ni1-N2	1.882(3)	S2-Ni2-S4	96.07(4)	Ni1-N2	1.887(3)	O5-Ni2-S4	91.82(9)
Ni1-S1	2.1820(11)	O1-C7-N1	126.4(4)	Ni1-S1	2.1828(12)	O6-Ni2-S4	97.69(9)
Ni1-S2	2.1895(10)	O1-C7-C6	117.8(4)	Ni1-S2	2.1697(13)	S2-Ni2-S4	166.05(5)
Ni2-S1	2.2331(10)	N1-C7-C6	115.6(3)	Ni2-O5	2.053(3)	O5-Ni2-S3	171.31(9)
Ni2-S3	2.2323(11)	C1-S1-Ni1	87.72(13)	Ni2-O6	2.070(3)	O6-Ni2-S3	96.15(9)
Ni2-S2	2.2354(11)			Ni2-S1	2.4877(13)	S2-Ni2-S3	88.94(4)
Ni2-S4	2.2464(10)			Ni2-S3	2.4495(12)	S4-Ni2-S3	79.52(4)
C7-O1	1.248(5)			Ni2-S2	2.4112(13)	O5-Ni2-S1	98.72(9)
C7-N1	1.348(5)			Ni2-S4	2.4302(13)	O6-Ni2-S1	170.41(9)
N2-Ni1-N1	89.16(14)			C7-O1	1.254(5)	S2-Ni2-S1	79.61(4)
N2-Ni1-S1	170.96(10)			C7-N1	1.354(5)	S4-Ni2-S1	90.76(4)
N1-Ni1-S1	91.70(11)			N2-Ni1-N1	87.99(15)	S3-Ni2-S1	80.87(4)
N2-Ni1-S2	91.51(10)			N2-Ni1-S2	89.39(11)	O1-C7-N1	124.8(4)
N1-Ni1-S2	174.89(11)			N1-Ni1-S2	175.73(11)	O1-C7-C6	117.6(4)
S2-Ni1-S1	86.85(4)			N2-Ni1-S1	177.93(11)	N1-C7-C6	117.6(4)
S3-Ni2-S1	94.58(4)			N1-Ni1-S1	90.33(11)	C1-S1-Ni1	97.67(14)
S3-Ni2-S2	175.61(4)			S2-Ni1-S1	92.22(5)		

Table 2 (continued). Selected Bond Distances [Å] and Bond Angles [deg] for the Complexes.

Complex **8**				Complex **10**			
Ni1-Ni2	3.4030(8)	O3A-Ni2-S1A	93.65(18)	Ni1-Ni2	2.8255(4)	S1-Ni1-Ni2	51.198(15)
Ni1-N1	1.898(5)	O3-Ni2-S1A	86.35(18)	Ni1-N1	1.8909(17)	P1-Ni2-P2	86.18(2)
Ni1-N2	1.895(5)	O3A-Ni2-S1	93.65(18)	Ni1-N2	1.8895(17)	P1-Ni2-S1	99.13(2)
Ni1-S1	2.1880(18)	O3-Ni2-S1	180.00(18)	Ni1-S1	2.1558(5)	P2-Ni2-S1	173.53(2)
Ni1-S2	2.1565(18)	S1A-Ni2-S1	84.15(18)	Ni1-S2	2.1438(5)	P1-Ni2-S2	172.59(2)
Ni2-O3	2.063(5)	O3A-Ni2-S2	95.85(18)	Ni2-P1	2.1781(6)	P2-Ni2-S2	99.44(2)
Ni2-O3A	2.063(5)	O3-Ni2-S2	103.50(5)	Ni2-P2	2.1816(6)	S1-Ni2-S2	75.585(19)
Ni2-S1	2.4412(16)	S1A-Ni2-S2	76.50(5)	Ni2-S1	2.2354(6)	P1-Ni2-Ni1	131.452(18)
Ni2-S1A	2.4412(16)	S1-Ni2-S2	95.85(18)	Ni2-S2	2.2413(5)	P2-Ni2-Ni1	124.842(18)
Ni2-S2	2.4537(18)	O3A-Ni2-S2A	84.15(18)	C7-O1	1.244(3)	S1-Ni2-Ni1	48.725(14)
Ni2-S2A	2.4538(18)	O3-Ni2-S2A	76.50(5)	C7-N1	1.359(3)	S2-Ni2-Ni1	48.387(14)
C7-O1	1.251(8)	S1A-Ni2-S2A	103.50(5)	N2-Ni1-N1	86.79(8)	O1-C7-N1	123.6(2)
C7-N1	1.336(9)	S1-Ni2-S2A	180.00(18)	N2-Ni1-S2	97.29(5)	O1-C7-C6	117.44(19)
N2-Ni1-N1	85.10(2)	S2-Ni2-S2A	100.2(2)	N1-Ni1-S2	175.92(6)	N1-C7-C6	118.61(18)
N2-Ni1-S2	93.56(16)	O1-C7-N1	125.3(6)	N2-Ni1-S1	176.58(6)	C1-S1-Ni1	111.15(7)
N1-Ni1-S2	174.77(16)	O1-C7-C6	117.1(6)	N1-Ni1-S1	96.64(6)		
N2-Ni1-S1	177.42(15)	N1-C7-C6	117.5(6)	S2-Ni1-S1	79.29(2)		
N1-Ni1-S1	92.79(17)	C1-S1-Ni1	100.2(2)	N2-Ni1-Ni2	126.55(6)		
S2-Ni1-S1	88.46(7)			N1-Ni1-Ni2	125.67(5)		
O3A-Ni2-O3	180.00(18)			S2-Ni1-Ni2	51.412(15)		