Supporting Information of

On $[Fe_4S_4]^{2+}$-(μ_2-SR)-M^{II} Bridge Formation in the Synthesis of an A-Cluster Analogue of Carbon Monoxide Dehydrogenase/-Acetylcoenzyme A Synthase

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Table S1. Crystallographic Data for Mononuclear and Binuclear Complexes and Clusters[a]

	1	(Bu_4N)[**2**]	**4**	[**5**]$(Ni(PPh_3)Cl_3)_2$	[**6**](PF_6)	[**7**](PF_6)
formula	$C_{32}H_{29}ClP_2PtS$	$C_{25}H_{48}N_2PdS_3$	$C_{11}H_{24}Cl_2FeN_2NiS_2$	$C_{58}H_{78}Cl_3N_4Ni_5P_2S_4$	$C_{29}H_{39}ClF_6N_2NiP_2PdS_4$	$C_{29}H_{39}ClF_6N_2NiP_2PtS_4$
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
fw	738.09	579.23	433.90	1527.67	856.25	944.93
space group	P2(1)/n	P2(1)/c	P2(1)2(1)2(1)	P2(1)/n	$P\bar{1}$	$P\bar{1}$
a, Å	11.840(5)	19.899(3)	8 .810(2)	9.5118(5)	8.537(3)	8.521(2)
b, Å	14.971(7)	9.562(2)	12.479(2)	15.7143(8)	14.338(5)	14.353(4)
c, Å	16.114(7)	15.329(2)	16.025(3)	21.725(1)	15.089(5)	15.153(4)
α, deg	90	90	90	90	98.508(9)	98.851(6)
β, deg	90.842(8)	94.378(3)	90	93.420(1)	101.711(9)	101.594(6)
γ, deg	90	90	90	90	106.176(7)	106.111(6)
V, Å^3	2856(2)	2897.3(7)	1761.8(5)	3241.5(3)	1695(1)	1700.4(8)
Z	4	4	4	2	2	2
T(K)	213	213	193	213	193	193
ρ_{calc}, g cm^{-3}	1.717	1.328	1.636	1.565	1.677	1.846
2θ range, deg	3.72 to 45.00	2.06 to 56.62	4.14 to 45.00	3.76 to 45.00	3.02 to 56.76	3.64 to 56.64
GOF (F^2)	1.195	1.026	1.098	1.349	0.988	1.032
R_1^b/wR_2^c	0.0700/0.1686	0.0486/0.1367	0.0709/0.1720	0.0517/0.0918	0.0634/0.1577	0.0551/0.1276

	[**8**](PF_6)	[**9**](PF_6)	[**10**](PF_6)	**13**·CH_2Cl_2	(Bu_4N)[**18**]·1.5CH_3CN·0.5Et_2O	$(Bu_4N)_3$[**21**]·3CH_3CN
formula	$C_{25}H_{38}F_6N_2Ni_2P_2S_3$	$C_{25}H_{38}F_6N_2NiP_2PdS_3$	$C_{25}H_{38}F_6N_2NiP_2PtS_3$	$C_{44}H_{42}Cl_2N_2NiO_2P_2PtS_2$	$C_{83}H_{119.5}Fe_4N_{4.5}NiO_{0.5}S_{15}$	$C_{160}H_{215}Fe_8N_7S_{27}$
crystal system	triclinic	triclinic	triclinic	orthorhombic	monoclinic	triclinic
fw	756.11	803.80	892.49	1081.56	1819.23	3548.81
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P2(1)2(1)2(1)	Cc	$P\bar{1}$
a, Å	9.888(2)	9.898(2)	9.731(3)	11.462(2)	21.048(2)	23.596(3)
b, Å	10.803(2)	10.935(2)	10.970(3)	14.999(3)	30.319(3)	24.803(3)
c, Å	15.035(3)	15.043(2)	15.100(4)	24.035(4)	31.941(3)	40.915(5)
α, deg	95.877(4)	94.906(4)	94.878(6)	90	90	86.471(2)
β, deg	96.162(4)	96.752(4)	96.693(5)	90	91.844(2)	80.242(2)
γ, deg	95.472(4)	94.115(4)	93.496(6)	90	90	64.576(2)
V, Å^3	1579.1(5)	1605.3(4)	1591.0(8)	4132(2)	20373(3)	21313(4)
Z	2	2	2	4	8	4
T(K)	193	193	193	193	193	213
ρ_{calc}, g cm^{-3}	1.590	1.663	1.863	1.739	1.272	1.106
2θ range, deg	2.74 to 45.00	2.74 to 50.00	2.72 to 56.66	3.20 to 45.00	2.52 to 45.00	2.32 to 45.00
GOF (F^2)	1.030	1.082	1.004	0.996	1.012	1.016
R_1^b/wR_2^c	0.0586/0.1778	0.0586/0.1633	0.0534/0.1398	0.0482/0.0974	0.0725/0.1991	0.0802/0.2517

[a]MoK_α radiation (λ = 0.71073 Å). [b]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$

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Table S2. Bond Distances (Å) and Angles (deg) of Complexes **4-7**

	4	**5**	**6**	**7**
Ni - N1	1.992(8)	1.982(4)	1.991(5)	1.987(7)
Ni - N2	1.985(8)	1.976(4)	1.990(5)	1.991(7)
Ni - S2	2.188(2)	2.173(2)	2.184(2)	2.165(3)
Ni - S1	2.177(3)	2.167(2)	2.160(2)	2.190(2)
Ni - M	2.796(2)[a]	2.7768(6)[b]	2.974(1)[c]	2.984(1)[d]
M - P1	-	-	2.282(2)	2.257(2)
M - Cl1	2.275(3), 2.222(3)	-	2.310(2)	2.321(2)
M - S2	2.410(3)	2.200(1)	2.292(2)	2.358(2)
M - S1	2.426(3)	2.216(1)	2.358(2)	2.282(3)
N1-Ni-N2	100.5(3)	100.4(2)	100.1(2)	100.1(3)
N2-Ni-S2	88.2(2)	89.3(1)	88.5(2)	88.5(2)
N1-Ni-S1	89.2(2)	89.0(1)	89.2(2)	89.5(2)
S1-Ni-S2	82.1(1)	81.27(5)	81.87(7)	81.51(9)
P1-M-Cl1	117.1(1)	-	86.92(7)	87.03(8)
S1-M-S2	72.7(1)	79.59(5)	75.48(6)	75.54(8)
dihedral angles between NiN1N2S1S2 and MS1S2P1Cl1	-[e]	112.14(7)	114.24(9)	114.6(1)
dihedral angles between NiS1S2 and MS1S2	101.86(9)	112.29(6)	117.35(7)	117.74(9)

[a]M = Fe. [b]M = Ni. [c]M = Pd. [d]M = Pt. [e]$FeCl_2/FeS_2$ dihedral angle = 86.16(8)°.

Table S3. Bond Distances (Å) and Angles (deg) of $[\{Ni(L_o\text{-}S_2N_2)\}M(SCH_2CH_2PPh_2)]^{1+}$

	M = Ni (**8**)	M = Pd (**9**)	M = Pt (**10**)
Ni - N1	1.966(6)	1.986(7)	1.975(7)
Ni - N2	1.988(6)	1.995(7)	1.986(7)
Ni - S2	2.155(2)	2.175(2)	2.174(2)
Ni - S1	2.161(2)	2.176(3)	2.188(2)
Ni - M	2.745(1)	2.844(2)	2.849(1)
M - P	2.142(2)	2.230(2)	2.228(2)
M - S3	2.156(2)	2.278(2)	2.283(2)
M - S2	2.229(2)	2.360(2)	2.354(2)
M - S1	2.229(2)	2.364(2)	2.364(2)
N1-Ni-N2	100.3(3)	100.4(3)	100.6(3)
N2-Ni-S2	89.4(2)	88.5(2)	88.5(2)
N1-Ni-S1	89.9(2)	89.2(2)	89.3(2)
S1-Ni-S2	80.32(7)	81.79(9)	81.41(9)
P-M-S3	87.70(7)	86.34(8)	86.83(8)
S1-M-S2	77.25(7)	74.17(8)	74.17(7)
dihedral angles between NiN1N2S1S2 and MS1S2S3P1	109.16(7)	106.72(9)	106.35(9)
dihedral angles between NiS1S2 and MS1S2	108.07(6)	107.19(8)	107.17(7)