Supplementary Information for

The Design of Earth Abundant Metal Catalysts for Nitrous Oxide-Based Oxidations. Part I. N_2O Coordination and Oxygen-Transfer to Metal

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*Table of Contents for non-XYZ files**

The X,Y,Z coordinates for all computed structures are in a separate Mercury-readable SI file named: KN LM-N2O_XYZ.xyz

Preparation of *N,N′*-bis(salicylideneamino)ethanato)iron (II) [(Salen)Fe].

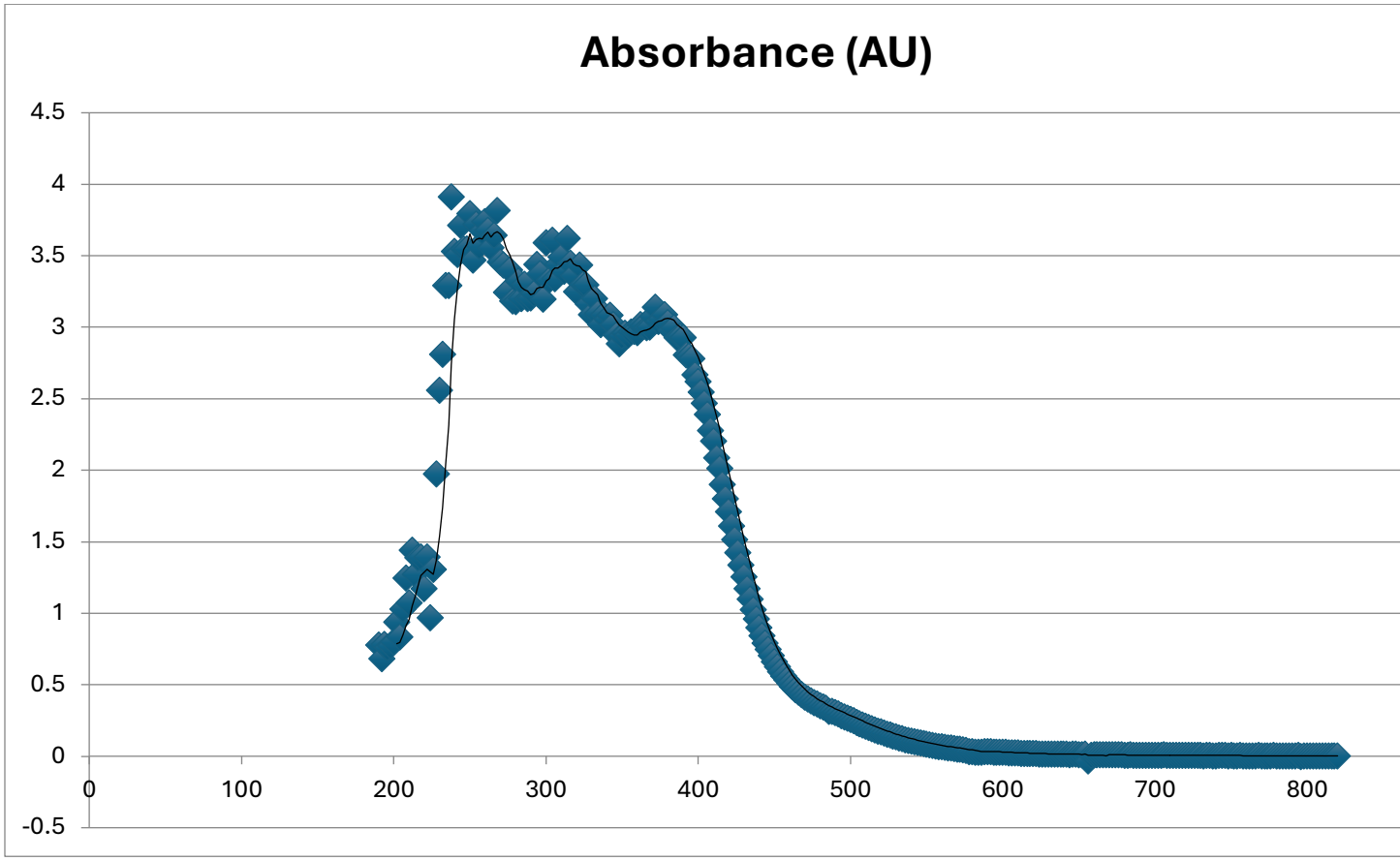
(Salen)Fe was prepared by the reaction of the N,N'-bis(salicylideneamino)ethane and iron(II) acetate in refluxing methanol under nitrogen by a literature method. (Earnshaw, A.; King, E. A.; Larkworthy, L. F. *J. Chem. Soc. A*: *Inorganic, Physical, Theoretical* **1968**, 5, 1048-52).

Experimental Procedure for Fe(Salen) Reaction with N_2O

Approximately 50 mg of dark red brown Fe(Salen) was transferred under nitrogen in an inert atmosphere box into a 150 mL Fisher-Porter thick-walled glass vessel fitted with a stir bar and then capped with a rubber septum. After transferring the vessel out of the box, 5 mL of dry N_2-saturated methylene chloride was injected through the septum with N_2 purging. The septum was replaced quickly with a N_2O-purging reactor head which was then attached to the glass reactor. Several cycles of N_2O pressurization/venting cycles were carried out as the reactor pressure was raised gradually to 90 psig with magnetic stirring; after a few hours an orange-rust colored solid gradually formed. After stirring at rt for 48 hr the N_2O was vented and the orange solid was allowed to settle. Under a N_2-purge the red supernatant solution was drawn off by syringe, and the orange solid (approx. 25 mg) was dried under an N_2 flow for characterization and storage. UV-Vis (CH_2Cl_2, λ) 250 nm, 314 nm, 386 nm; ESI-MS (MeOH or CH_2Cl_2), M/e 322.0405 [$C_{16}H_{14}N_2O_2Fe^+$=(Salen)Fe^+], 675.0985 [$C_{32}H_{29}N_5O_5Fe_2^+$= (Salen)$_2Fe_2(NO)H^+$], 689.0782 [$C_{32}H_{29}N_6O_5Fe_2^+$=(Salen)$_2Fe_2(N_2O)H^+$]; each of these ions appeared as a cluster of peaks with the appropriate iron isotopic signature, ^{54}Fe (6%), ^{56}Fe (92%), ^{57}Fe (2%). Initial efforts to grow X-ray quality crystals of this product were unsuccessful. UV-Vis and ESI-MS (experimental and simulated) spectra are on following pages.

A control experiment in which an Fe(Salen) solution in methylene chloride was stirred in air did not show a similar color change nor formation of a precipitate.

UV-Vis spectrum: Fe(Salen) + N_2O rxn and soln in CH_2Cl_2



Spectrum Plot Report

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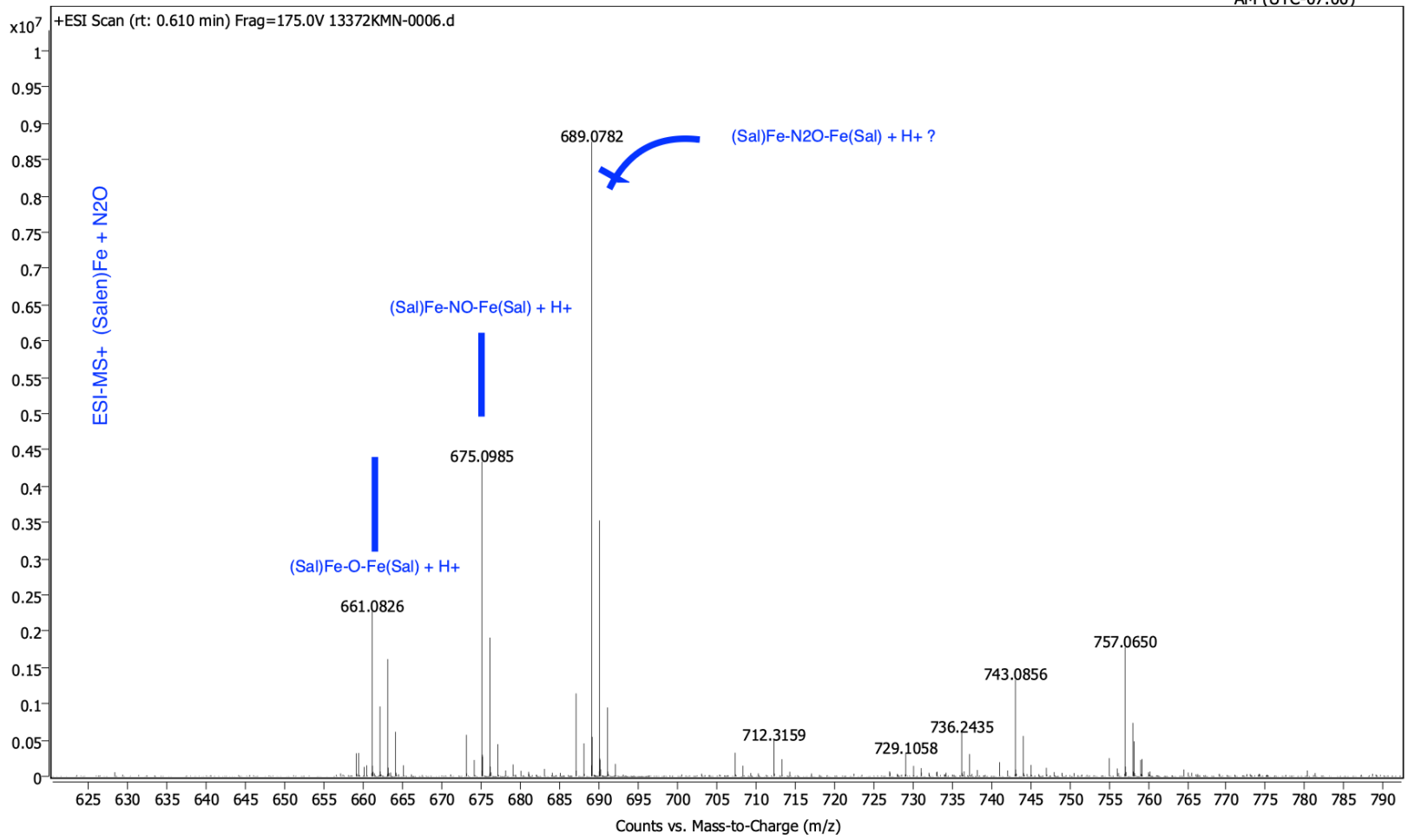
Name	KN-7-10	Rack Pos.		Instrument	G6546A QTOF	Operator	
Inj. Vol. (ul)	5	Plate Pos.		IRM Status	Success		
Data File	13372KMN-0006.d	Method (Acq)	Pos-Loop-SF-6546.m	Comment	0.01x	Acq. Time (Local)	7/10/2024 10:24:17 AM (UTC-07:00)



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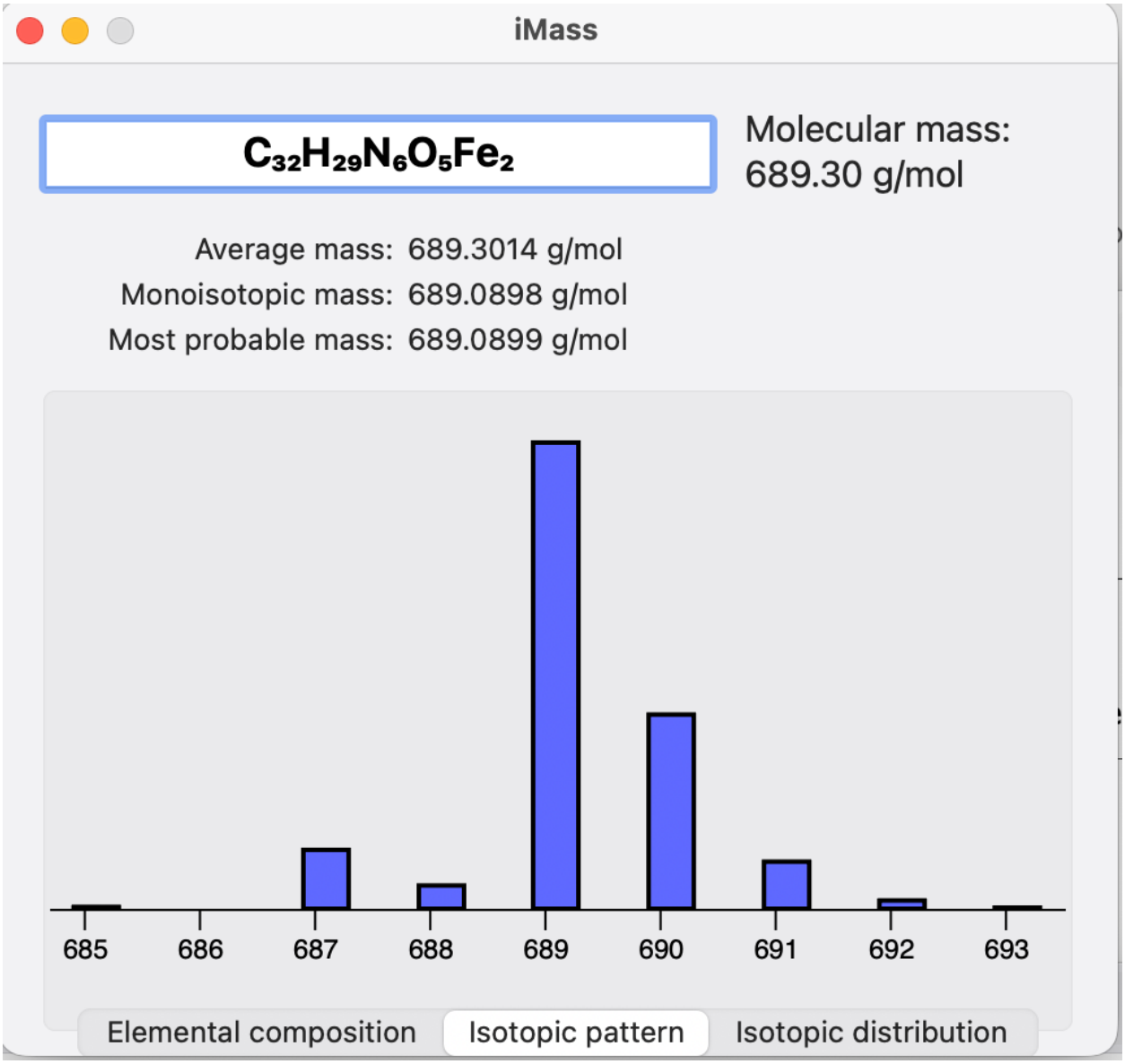
Simulated MS for (Salen)2Fe2(N2O)H+



LM	G LM	G(LM+ N2O)	G LM(N2O)	ΔGa	LM-ON2 G* O-N	ΔG* O-N	G LM-N2O-ML	G* M-N2-O-M	ΔG* M-N2-O-M	G LM-N2O-M	ΔG O-transf	G LMO
(POR)Fe (9)	-1111.60247	-1296.26828	(N) -1296.27596	-4.5						s,s -6.1	-25.3	t -1186.80786
L=O (s)			(O) -1296.26803	0.5	-1296.23067	23.4						
(t)	-1111.63573		(O) -1296.29323	5.5	-1296.25711	22.7	b,t -2407.88092	-2407.88273	0-1	s,t +14.8		
			(N) -1296.29115	6.8						(b) t/q +25.2	tDS -24.1	t,D,S -1186.89273
(q)	*-1111.64456*	-1296.31087	(N) -1296.30347	4.6			b,q -2407.89762	-2407.89382	2.4	(b) q/q +36.3		q -1186.79419
			(O) -1296.30760	2.1	(q) -1296.26138	29						
D3 disp			(O) -1296.35425									q,D,S
(q) D,CH2Cl2	-1111.72383	-1296.38784	(N) -1296.38549	1.5			t -2408.06444	t -2408.06166	1.7			
			(O) -1296.38502	1.8	q -1296.34444	25.4	q -2408.07849			q/q +22.0		
(dipyr-dimin)Fe (15)												
L=0 (s)	-846.02746	-1030.69377	-1030.71178	-11.3								
			(O) -1030.70417	-6.5	(s) -1030.6702	21.3						
OPBE	-845.99286		-1030.60817	-4								
L=0 (t)	*-846.09152*	-1030.75783	(N) -1030.75300	3								(t) -921.24838
			(O) -1030.75314	2.9	(t) -1030.70829	28	(b,t) -1876.77877	xxxxxxxx	2.8	41.3		
t,D,CH2Cl2	-846.15499	-1030.81898	(O) -1030.81714	1.2	(t) -1030.76547	32.4					-21	(t) -921.31895
(q)	-846.07277	-1030.74314	(N) -1030.74556	-1.5			(b,q) -1876.79164	-1876.79085	0.5	33.1		XXXXXX
			(O) -1030.74936	-4								
q,D,CH2Cl2							(q) -1876.93808	-1876.93463	2.2	20.1		
(N-4Py)Fe(2+) (3)												
(s)	*-1285.5119*	-1470.17814	(N) -1470.18821	-6.3								(s) -1360.65139
			(O) -1470.17747	0.4	(s) 1470.13368	27.5						
(t)	-1285.51138	-1470.17769	(O) -1470.17704	0.4	(t) -1470.13858	24.1						(t) -1360.70025
CH2Cl2 (s)	-1285.70519	-1470.37329	(N) -1470.37281	0.3								
			(O) -1470.3977									
s,D,CH2Cl2	-1285.81092		(N) -1470.48582	-6.8								
			(O) -1470.47178	2	(s) -1470.4284	27.2						
t,D,CH2Cl2	*-1285.81124*		(O) -1470.46711	4.5	(t) -1470.44241	15.5					-36.5	t,D,S -1360.99979
(CN)5Fe(3-) (8)												
(s)	(i) -587.50828	-772.17459	(N) -772.196	s,s -13.4			dissoc					(s) -662.66008
			(O) diss									
(t)	*(i) -587.53065*	-772.19696	(N) xxxx	t,s 0.6								(t) -662.70845
			(O) DNC									(q) dissoc
L=NH3 (s)	-644.05046	-828.71677	(N) -722.196	-5.9			dissoc					
D,H2O	-644.65751	-829.3215	-772.76929	10								t,D,S -663.2978
(t) DNC												
(s) in H2O	-588.10239	-772.75676	(N) -772.76408	-4.6			l,s -1360.84667	DNC		3.7	-51.7	-663.28698
			(O) -772.75828	7.8	-772.71194	29.1						
D,H2O	*(t) -588.11893*	-772.77387	s (O) -772.77339	t,s 0.3	-772.72058	33.1	t -1360.82747	xxxx		40.7	-30.4	t,D,S -663.2978
	(s) -588.08946		s (N) -772.77277	t,s 0.7								
L=H2O (s) in H2O	(s) -664.51446	-849.18277		4.9								
D,H2O	(s) -664.53358	-849.19945	(N) -772.77449	5.1			l,s -1360.87516			10.3		
(H-salen)Fe (12)												

(q)	*-1001.38669*	-1186.0494	(O) -1186.04361	3.6	(q) -1186.00495	24.4	(l) -2187.40910		(l-b) 29.1	14.7		(q) -1076.53271
			(N) -1186.04333	3.8			(b) -2187.36375	-2187.36258	0.7	39.3		
D=disp	D) -1001.41668	1186.08324	(D) -1186.08168	1			(b,D) -2187.46447			(D,q) 21.3		
q,D,CH2Cl2	*-1001.45107*	-1186.11506	(O) -1186.11043	2.9	(q) -1186.07616	22.1	(l) -2187.55861	(l-b=21.7)		(q) 3.2 ??		q,D,S -1076.60454
			(N) -1186.11012	3.1			(b) -2187.52405	-2187.51756	4.1	(t,q) 1.1		
(t)	-1001.37975		(O) -1186.03894	4.5	-1185.99196	29.5	(b) -2187.34691			(t,l) 23.1		(t) -1076.53535
			(N) d -1186.08357				(l) -2187.38902					
t,D,CH2Cl2	-1001.44822	-1186.11221	(O) -1186.10863	2.2	-1186.05801	31.8					q/t -19.1	t,D,S -1076.61192
(sal-OPrO)Fe (13)												
(t)	-1004.16129	-1183.8276	(O) -1188.81928	5.2								
(q)	*-1004.18829*	-1188.8546	(O) -1188.84471	6.2								
			N -1188.84478									
q,D3,CH2CL2	-1004.25692	-1188.92384	(O) -1188.91343	6.5								
			N -1188.91334	6.6								
(N-3Pyr)M												
M=V (t) (1a)	-870.76114	-1055.42745	(N) -1055.43207	(N) -2.9	(s) -1055.36374	(t,s) 40.3						
			(O) -1055.42801	(O) -0.1	CP -1055.40339	15.4					xxxxx	(s) -946.00799
(t,D3,CH2Cl2)	-870.84612	-1055.51011	(N) -1055.51225	(N) -1.4		(t,s) 40.9					-114.9	D,S -946.07854
			(O) -1055.50147	(O) 5.4	cp -1055.47976	13.6						
(t,M06,CH2Cl2)	-870.76498	-1055.39822	(N) -1055.39799	(N) 0.1								
t,OPBE,CH2Cl2			DNC									
					chk expt							
M=Fe(t) (1b)	-922.87258	-1107.53889	(N) -1107.55071	(N) -7.4	(t) -1107.50398	29.2						
			(O) -1107.53635	(O) 1.6								
(t) CH3CN			(N) -1107.62204									(t) -998.06494
(t) D CH2Cl2	-923.00418	-1107.66819	(N) -1107.67732	(N) -6.4								
			(O) -1107.66469	(O) 2.2	(t) -1107.62762	23.3						
(t) M06(solv)				(N) -8.2								
				(O)								(q) -998.09106
(q)	*-922.91117*	-1107.57748	b (N) -1107.57024	(N) 4.5							-29.9	(q) -998.21799
			d (O) -1107.5694	(O) 5.1	qn) -1107.53613	25.9						
q,D,CH2Cl2	*-923.03995*	-1107.70394	(N) -1107.69735	4.1								
			(O) xxx		qn,sol -1107.6635	26						
M=Mn (q) (1d)	-903.35583	-1088.02214	(N) -1088.03049	(N) -5.2								(d) -978.57493
			(O) -1088.01763	(O) 2.8	est -1088.01129	est 4.0						(q) -978.59124
q,D,CH2Cl2	*(q) -903.48145*	-1088.14732	(N) -1088.15673	(N) -5.9								(st) -978.56150
			(O) -1088.14602	(O) +0.8	est -1088.13949	est 4.1					-67.2	q,D,S -978.71898
(sext)	*-903.41536*	-1088.08167	(N) -1088.07430	(N) 4.6								
			(O) -1088.07452	(O) 4.5	est -1088.04629	est 17.7						
sxt,D,CH2Cl2	*-903.54823*	-1088.2141	(N) -1088.20582	(N) +5.2								
			(O) -1088.20664	(O) +4.7	est -1088.17167	est 21.9						
M=Cr (t) (1c)	-885.73377	-1070.40008	b (N) -1070.44116	t,t (N) -25.8								(t) -961.01834
			(O) dissoc									(s) -960.97528
(s)	-885.71041		(s) -1070.40708									(q) -960.95475
(q)	*-885.77628*	-1070.44259	(q,N) -1070.43945	b(N) q 1.9								

			(q,O) -1070.44525	b q(O) -1.7	(q) -1070.44947	2.6				-67.2	t,D,S -961.14032
D,CH2Cl2	*(q) -885.90275*	-1070.56862	(q) N -1070.5641	b,q (N) 2.8							
			(O) -1070.5708	b,q (O) -1.4	(q) -1070.5728	ca. -1.2					
Cr(POR)(Py) (t) (11)	-1322.71584	-1507.38215	(O) -1507.39759	(O) -9.7	(t) -1507.38109	10.4					(t) -1397.94015
BP86	-1322.92078		(N) -1507.40123	(N) -12.0							(s) -1397.93993
D,CH2Cl2	-1322.81627	-1507.48214	(O) -1507.4758	(O) 3.4	-1507.49135	5.6				-65.1	(t) -1398.04942
			(N) -1507.50529	(N) -14.5						-62.8	(s) -1398.04573
(s)			(N) -1507.32836								
			(O) -1507.33587								
(q)	*-1322.72645*		b (O) -1507.39681								
BP86	*-1322.93482*		(N)								
(N-2Pyr-Py)Fe (2)											
(q)	*-961.53799*	-1146.2043	(N) -1146.20581	-1							(q) -1036.72187
			(O) -1146.20590	-1	(q) -1146.17125	21.8					(t) -1036.70053
(t)	-961.51066	-1146.17697	(N) -1146.18678	-6.7							
q,D,CH2Cl2	-961.63432	-1146.29831	(O) -1146.29076	(O) 4.7	(q) -1146.25418	23				-27.1	q,D,S -1036.80797
			(N) -1146.29472	(N) 2.3							
(TPM)FeCl2 (s) (4)	-1759.33566	-1944.00197	(N) -1944.00142	0.3							
			(O) -1944.00091	0.7	(s) -1943.95235	30.5					
s,D,CH2Cl2	-1759.44577	-1944.11164	(N) -1944.10986	s,s 1.1							(s) -1834.46076
			(O) -1944.10658	3.1	-1944.05602	31.7					
(t)	*-1759.34667*	-1944.01298	(N) -1944.00144	7.2							(t) -1834.50836
			(O) -1943.99719	9.9							
t,D,CH2Cl2	*-1759.45698*	-1944.12097	(N) -1944.11584	t,t 3.2						-18.4	t,D,S -1834.61674
			(O) -1944.09957	tt 13.4							
Ru(NH3)5(2+) (7)											
(s)	-376.0639	-560.73021	(N) -560.74831	-11.3							
			(O) -560.73728	-4.4							
s,D,H2O	-376.39131	-561.0571	(N) -561.06241	-3.3							
			(O) -561.05049	4.4							
Cu(TPB) (5)											
(s)	-898.41276	-1083.07907	(O) -1083.07545	2.3	-1083.01922	35.5	(s) -1981.4885	(t) -1981.45626	20.2		(s) -973.50611
			(N) -1083.08384	-3							(t) -973.54885
s,D,CH2Cl2	-898.46712	-1083.13299	(O) -1083.12629	4.2	-1083.07273	33.6	(s) -1981.59699	(t) -1981.56831	18	-4.8	(t) -973.60037
			(N) -1083.13545	-1.5							
Ru(NH3)5(H2O)2+	-452.49948		(N) -560.74831	9							
s,D,H2O	-452.81288		(N) -561.06241	-2.4							
Ru(NH3)5(H2O)2Cl											
(s)	-1373.56676	-1558.23307	+H2O -1558.2241	5.6							
s,D,H2O	-1373.66942	-1558.33529	-1558.33044	3							
(POR)RuCl (10b)										xxx	
(d)	(d) -1542.32717	-1726.99348	(N) -1726.98299	6.6			(t) -3269.27605	(t) -3269.27615	0 ?		(q) -1507.20657
			(O) -1726.98424	5.8							
D,CH2Cl2?	(d) -1542.42249	-1727.08836	(N) -1727.07234	10.1	xxxxxx						

			(O) -1727.07659	7.4									
Ru(salen)													
(s)	-971.76718	-1156.43349	d (O) -1156.42660	4.3			(s) -2128.18464	(s) -2128.1844	0.1	15			
			(N) -1156.42362				(t) -2128.21244	(t) -2128.2090	2.1	6.8			
(t)	*-971.78199*	-1156.4483	d (N) -1156.44031								-42.3	(t) -1273.14618	
			d (O) -1156.44135	4.4							t,D,S -43.6	t,D,S -1273.25184	
L'=imid (t) **(14b)**	(t) -1197.94403	-1382.61034	(N) -1382.55649	34.3							-24.5		
(s)	*(s) -1197.94765*	-1382.61396	(N) -1382.61984	-3.7	-1382.58073	19.8	(l,s) -2580.56632	(s) -2580.5506	9.8	1.5		(s) -1273.11769	
			(O) -1382.61226	1									
D,CH2Cl2	(s) -1198.05195	-1382.71826	(N) -1382.72064	-1.5			(l,s) -2580.7764	(s) -2580.7688	(D,sol) 4.7	-5.3			
			(O) -1382.71071	4.7	-1382.68311	17.3							
Ru(salen)Cl (14a)											-14.6	(d) -1507.21482	
(d)	-1432.04227	-1616.70858	(O) -1616.70139	4.5	(d) -1616.66599	22.2	(b,s) -3048.70569	(s) -3048.70498			-29.5	D,S -1507.30513	
			(N) -1616.70289	3.6			(b,t) -3048.71472	(t) -3048.71227	1.5	21.2			
D,CH2Cl2	-1432.12774	-1616.79173	(N) -1616.78947	1.4								(q) -1507.20657	
			(O) -1616.78622	3.5	(d) -1616.7525	21.2	(t) -3048.89987	(t) -3048.9007	-0.5	11.8			
Ru(POR)(THF)(10a)												(s) -1389.58739	
(s)	-1314.4119	-1499.07821	(N) -1499.09023	(t/s) -3.9		17.2						(t) -1389.61971	
			(O) -1499.07603	5	(s) -1499.04854							(s) -1232.40610 RuO2	
(t)	*-1314.41776*	-1499.08407	(N) -1499.03191										
			(O) ??????										
s,D,CH2Cl2	*-1314.52411*	-1499.1881	(N) -1499.19968	(s/s) -7.3							-47.4	t,D,S -1389.73004	
			(O) -1499.18338	3	(s) -1499.1571	16.5							
t,D, CH2Cl2	-1314.52114			t,s xxxx									
N2O B3LYP vac	-184.66631												
N2O D,CH2Cl2	-184.66399												

se noted; D = D3 dispersion, SMD solvation for CH2Cl2 or H2O as noted
ities indicated as s, d, t, q, qn, sxt