Thioether-ligated iron(II) and iron(III)-hydroperoxo/alkylperoxo complexes with an H-bond donor in the second coordination sphere

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Supporting Information

Crystallographic Information:

All reflection intensities were measured at 100(2) K (compound **3**) using a SuperNova diffractometer (equipped with Atlas detector) with Cu *K*α radiation (mirror optics, λ = 1.54178 Å) or at 110(2) K (compounds **1** and **8**) K using a KM4/Xcalibur (detector: Sapphire3) with enhance graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å) under the program CrysAlisPro (Versions 1.171.35.11 (**1** and **8**) or 1.171.36.24 (**3**) Agilent Technologies, 2011-2013). The same program was used to refine the cell dimensions and data reduction. The structure was solved with the program SHELXS-97 or SHELXS-2013 and was refined on F^2 with SHELXL-97 or SHELXL-2013.[1] Analytical numeric absorption corrections based on a multifaceted crystal model were applied using CrysAlisPro. The temperature of the data collection was controlled using the system Cryojet (manufactured by Oxford Instruments). The H atoms were placed at calculated positions using the instructions AFIX 13, AFIX 23, AFIX 43 or AFIX 137 with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C or N atoms. For compound **3**, the H atom of the amide group (*i.e.*, H atom attached to N6) was found from difference Fourier map, and its coordinates and isotropic temperature factor were refined freely.

1: The structure is ordered

3: The structure is mostly ordered. At the sixth coordination site (axial position), there is a mixture of F^- / N_3^-. This site disorder was modeled with occupancy factors of 67% for F^- and 33% for N_3^-. All refined occupancy factors are provided in the CIF file. The crystal lattice contains some amount of solvent molecules (MeCN). The two MeCN molecules per asymmetric unit are found to be located at sites of two-fold axial symmetry, and thus their occupancy factors must be 0.5.

8: The structure is mostly ordered except for one of the two BF_4^- counterions, which is found to be disordered over two orientations (occupancy factors for the major components: 0.574(4)). The structure also contains some very disordered lattice acetonitrile solvents molecules with occupancies likely to be lower than 1; their contributions were then taken out using the program SQUEEZE for the final refinement (all details about the SQUEEZE procedure have been embedded in the cif file).

Density Functional Calculations

Methods:

Density functional theory calculations were performed using the *Gaussian*-09 and *Orca* software packages.[2] We used the unrestricted hybrid density functional method UB3LYP-D with dispersion correction due to Grimme.[3-5] Geometries were optimized without constraints using the LACVP basis set on iron and 6-31G on the rest of the atoms in *Gaussian*-09 and an equivalent set, LANLDZ basis set on iron and 6-31G on the rest of the atoms in *Orca* comprised of the auxiliary basis sets def2-SVP/J and def2-SVP/K for the RIJCOSX approximation.[6-8] Subsequently, improved energies were obtained at single point level with an LACV3P+ basis set on iron and 6-311+G* on the rest of the atoms in *Gaussian*-09.[6,7]

Geometry optimizations converged to local minima with real frequencies only. Although we calculated $[Fe^{III}(N3Py^{amide}SR)(OOH)]^{2+}$ in the lowest lying doublet, quartet and sextet spin states, under all conditions the doublet spin state was the ground state which matches the experimental data and provides a good calibration of our method. Subsequent calculations for all other species were preformed on the doublet spin state only. This is in good agreement with DFT calculations of the iron(III)-hydroperoxo species in heme enzymes, such as cytochrome P450, where also a doublet spin ground state was found.[9] By contrast, in non-heme iron(III)-hydroperoxo complexes with trigonal bipyramidal conformation typically a high-spin ground state is found.[10]

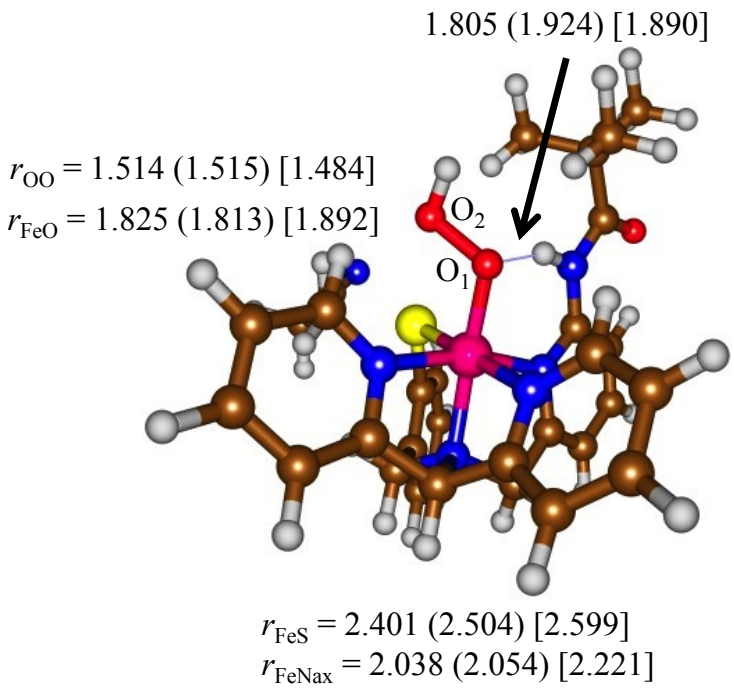

Figure S1. Optimized geometries of ^{2,4,6}[Fe^{III}OOH(N3Py^{amide}SR)]$^{2+}$ (**5**) as calculated with UB3LYP-D in *Gaussian*-09 with bond lengths in angstroms.

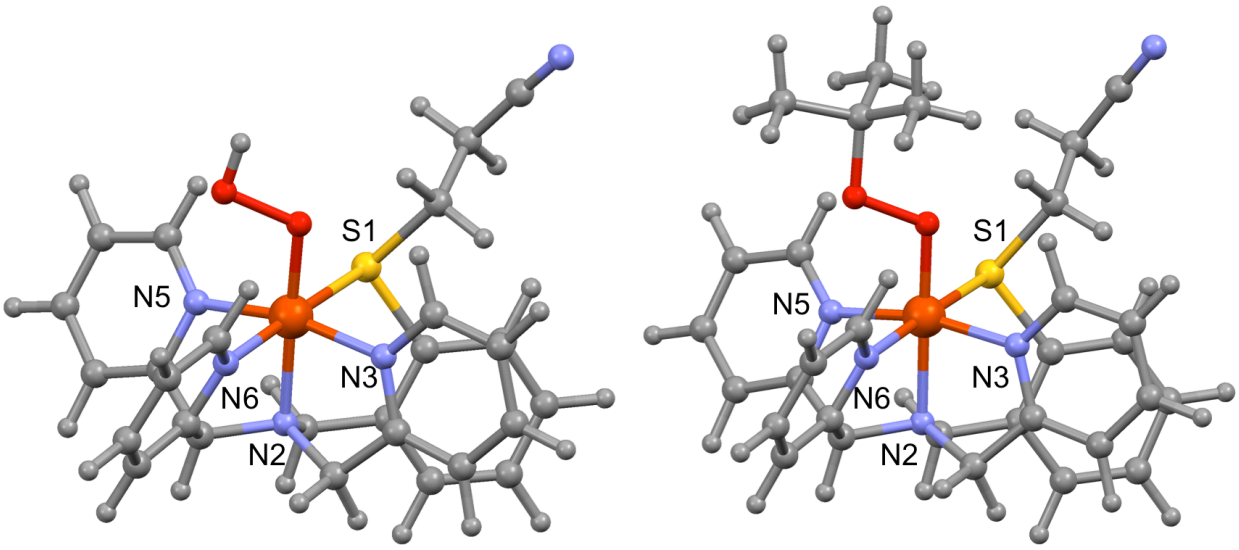

Figure S2. Optimized geometries of ^{2}**4** (left) and ^{2}**6** (right) as calculated with UB3LYP-D in *Orca*. Relevant bond distances are given in Table S1.

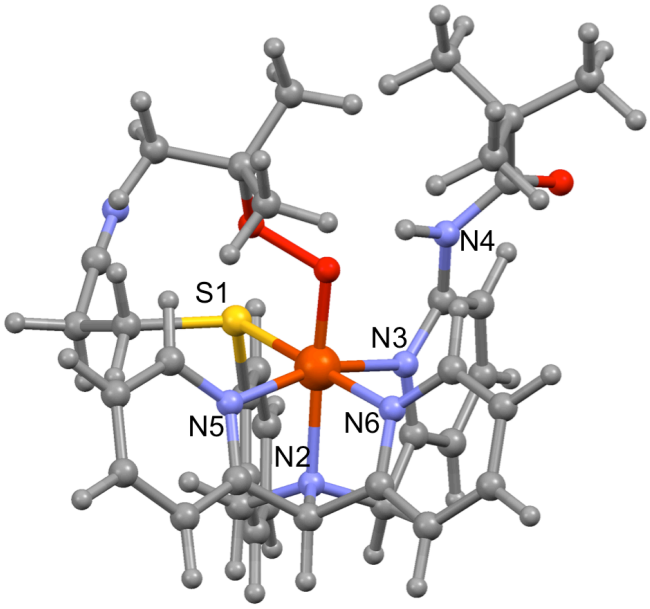

Figure S3. Optimized geometry of ^{2}**7**, as calculated with UB3LYP-D in *Orca*. Relevant bond distances and angles are given in Table S1.

Table S1. Selected bond distances (Å) and angles (°) for DFT structures calculated in *Orca*.[a]

	^{2}**4**	^{2}**5**	^{2}**6**	^{2}**7**
Fe-O	1.81	1.83	1.80	1.82
Fe-N2	2.06	2.04	2.06	2.06
Fe-N3	1.98	2.03	1.98	2.04
Fe-N5	1.96	1.98	1.96	1.97
Fe-N6	1.99	2.01	1.98	2.02
Fe-S1	2.43	2.39	2.43	2.39
N4-O	N/A	2.74	N/A	2.82
N4-H--O	N/A	158.4	N/A	153.3

[a] calculated with UB3LYP-D in *Orca*.

Table S2. Absolute and relative energies, zero point energies and free energies from optimized geometries of ^{2,4,6}**5**, as calculated at the UB3LYP-D level of theory in *Gaussian*-09. Absolute energies are in au and relative energies are in kcal mol^{-1}.

(**a**)

LACVP basis set						
Multip	E	E+ZPE	G	ΔE^a	$\Delta E+ZPE^a$	ΔG^a
^{2}**5**	-2315.480194	-2314.843475	-2314.914353	0.00	0.00	0.00
^{4}**5**	-2315.459681	-2314.825428	-2314.897378	12.87	11.32	10.65
^{6}**5**	-2315.460588	-2314.827056	-2314.902791	12.30	10.30	7.26

[a] with respect to ^{2}**5**.

(**b**)

LACV3P+* basis set				
Multip	E	E+ZPE	ΔE^a	$\Delta E+ZPE^a$
^{2}**5**	-2316.379551	-2315.742832	0.00	0.00
^{4}**5**	-2316.363612	-2315.729359	10.00	8.45
^{6}**5**	-2316.374026	-2315.740494	3.47	1.47

[a] with respect to ^{2}**5**.

Table S3. Group spin densities and group charges of UB3LYP-D optimized geometries of ^{2,4,6}**5.** ^{2}**5**, ^{4}**5**, ^{6}**5** = doublet, quartet and sextet spin states respectively in *Gaussian*-09.

	Spin densities					Charges				
	Fe	O_1	O_2H	S	Rest	Fe	O_1	O_2H	S	Rest
^{2}**5**	0.91	0.16	0.01	-0.03	-0.05	0.50	-0.37	0.04	0.60	1.23
^{4}**5**	2.76	0.09	0.00	-0.01	0.16	0.64	-0.37	0.05	0.54	1.13
^{6}**5**	3.97	0.36	0.07	0.14	0.47	0.79	-0.42	0.09	0.49	1.05

Table S4. Group spin densities and group charges of UB3LYP-D/LACV3P+*//UB3LYP-D/LACVP calculations of ^{2,4,6}**5.** ^{2}**5,** ^{4}**5,** ^{6}**5** = doublet, quartet and sextet spin states respectively in *Gaussian*-09.

	Spin densities					Charges				
	Fe	O_1	O_2H	S	Rest	Fe	O_1	O_2H	S	Rest
^{2}**5**	0.94	0.14	0.01	-0.03	-0.06	0.16	-0.27	-0.01	0.48	1.64
^{4}**5**	2.83	0.06	0.00	-0.01	0.12	0.31	-0.29	0.05	0.39	1.54
^{6}**5**	4.12	0.29	0.06	0.14	0.38	0.31	-0.31	0.09	0.35	1.55

Table S5. Group spin densities and group charges of UB3LYP-D2 optimized geometries of ^{2}**4,** ^{2}**6,** ^{2}**7** in *Orca*.

	Spin densities					Charges				
	Fe	O_1	O_2R^a	S	Rest	Fe	O_1	O_2R^a	S	Rest
^{2}**4**	0.85	0.21	0.02	-0.02	-0.06	0.57	-0.38	0.05	0.57	1.19
^{2}**6**	0.77	0.26	0.04	-0.01	-0.06	0.54	-0.37	0.15	0.56	1.12
^{2}**7**	0.85	0.20	0.02	-0.02	-0.05	0.49	-0.37	0.12	0.61	1.15

^{a}R = H for ^{2}**4**, R = tBu for ^{2}**6** and ^{2}**7**

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Cartesian Coordinates:

Gaussian Optimized Geometries:

^{2}5:

26	0.100658000	0.084331000	0.005221000
16	0.115724000	-0.008359000	2.404593000
6	0.535140000	-0.867202000	5.432925000
6	0.439425000	-1.976660000	4.486571000
1	-0.603238000	-2.314313000	4.441466000
1	1.031625000	-2.828760000	4.845922000
6	0.942074000	-1.607163000	3.082075000
1	0.757820000	-2.423601000	2.383941000
1	2.000891000	-1.344722000	3.077314000
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6	-4.351501000	-0.427320000	3.604032000
1	-5.392557000	-0.511807000	3.894233000
6	-3.873379000	-1.154702000	2.506598000
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1	2.988979000	3.003666000	-0.429255000
1	4.310291000	4.167806000	-0.247913000
1	2.812449000	4.658122000	-1.048665000
6	3.133798000	6.014711000	1.355743000
1	4.227129000	6.061633000	1.369442000
1	2.752145000	6.407924000	2.300709000
1	2.765892000	6.662525000	0.554381000
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6	2.068527000	-2.230224000	0.040445000
1	2.701536000	-1.550892000	0.592542000
6	-0.788089000	-0.723871000	-2.508310000
6	-1.014841000	-0.773307000	-3.877865000
1	-1.596101000	-1.577579000	-4.313337000
6	-0.473075000	0.247275000	-4.678288000
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7	0.857509000	-1.744571000	-0.315161000
7	-0.064518000	0.279857000	-1.944194000
8	0.454208000	5.483862000	1.498595000
1	3.481455000	0.991863000	0.775113000
8	1.723298000	0.910450000	-0.085114000
8	2.667993000	0.490828000	1.021413000

^{4}5:

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6	2.314580000	-1.373582000	-0.957265000
6	3.590513000	-1.824139000	-1.275314000
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6	-0.052123000	-0.501304000	-4.764763000
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8	0.885903000	2.498773000	1.032979000

^{6}5:

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1	3.216252000	-1.248930000	4.562250000
6	1.967621000	-0.231767000	3.148690000
1	2.533273000	-0.574936000	2.284485000
1	2.267787000	0.786412000	3.406707000
6	-0.653964000	-1.652358000	2.952736000
6	-1.558957000	-1.693263000	4.017449000
1	-1.727994000	-0.809904000	4.621536000
6	-2.221420000	-2.892093000	4.316442000
1	-2.916964000	-2.926833000	5.147037000
6	-1.965172000	-4.037701000	3.557480000
1	-2.463102000	-4.971214000	3.794876000
6	-1.055713000	-3.983984000	2.493957000
1	-0.853916000	-4.881453000	1.916483000
6	-0.391151000	-2.790023000	2.165243000
6	0.563227000	-2.766494000	0.995277000
1	0.765272000	-3.794750000	0.666731000
1	1.518213000	-2.313873000	1.268046000
6	-1.359166000	-2.415298000	-0.558408000
1	-1.518951000	-3.463477000	-0.288863000
1	-1.469424000	-2.341042000	-1.644082000
6	-2.411252000	-1.543959000	0.087372000
6	-3.650375000	-2.065718000	0.413177000
1	-3.840896000	-3.126342000	0.305702000
6	-4.650865000	-1.191305000	0.872618000
1	-5.629823000	-1.574254000	1.136856000
6	-4.397054000	0.167033000	0.977877000
1	-5.152365000	0.868353000	1.296729000
6	-3.112591000	0.659347000	0.647143000
6	-3.661468000	3.093157000	0.910385000
6	-2.997151000	4.476967000	0.844763000
6	-2.275868000	4.662876000	-0.518494000
1	-1.434284000	3.972395000	-0.653108000
1	-1.882181000	5.683216000	-0.577977000
1	-2.975723000	4.527608000	-1.350847000
6	-4.094317000	5.551868000	0.991409000
1	-3.637001000	6.546139000	0.969985000
1	-4.638092000	5.434480000	1.932186000
1	-4.822227000	5.483741000	0.177768000
6	-1.985707000	4.603347000	2.016839000
1	-1.192535000	3.846915000	1.973238000
1	-2.492357000	4.498763000	2.982077000
1	-1.522457000	5.595851000	1.987012000
6	1.007070000	-2.024046000	-1.351044000
1	1.211613000	-3.051126000	-1.672786000
6	2.282056000	-1.323628000	-0.899063000
6	3.574890000	-1.753525000	-1.178503000
1	3.743941000	-2.699088000	-1.680392000
6	4.650896000	-0.932779000	-0.801767000
1	5.669022000	-1.244898000	-1.004608000
6	4.397969000	0.292992000	-0.173571000
1	5.208546000	0.952816000	0.110007000
6	3.075780000	0.662768000	0.088567000
1	2.805335000	1.592072000	0.573228000
6	0.423451000	-1.198036000	-2.492062000

6	0.480600000	-1.541064000	-3.838805000
1	0.915109000	-2.484491000	-4.148924000
6	-0.035899000	-0.637476000	-4.783039000
1	-0.003171000	-0.879849000	-5.839223000
6	-0.591146000	0.574560000	-4.352524000
1	-0.991374000	1.288194000	-5.061946000
6	-0.622801000	0.856452000	-2.983706000
1	-1.035908000	1.774706000	-2.585459000
7	0.751857000	-0.445432000	6.419476000
7	0.032184000	-1.985939000	-0.193136000
7	-2.121231000	-0.206705000	0.232190000
7	-2.784697000	1.999931000	0.698097000
1	-1.809464000	2.234699000	0.529853000
7	2.046914000	-0.146369000	-0.258958000
7	-0.122649000	-0.020858000	-2.085457000
8	-4.868984000	2.924876000	1.131880000
1	0.774782000	3.674652000	0.973051000
8	0.027108000	2.110465000	0.100957000
8	0.947612000	2.711383000	1.097328000

Orca Optimized Geometries:

^{2}4:

26	0.042620000	0.138099000	-0.062918000
16	1.352259000	0.743369000	-2.021181000
6	2.867158000	-0.403162000	-1.940523000
6	4.083177000	0.189054000	-2.681771000
6	5.200137000	-0.743794000	-2.513282000
7	6.039314000	-1.541642000	-2.336152000
1	3.872489000	0.335960000	-3.748508000
1	4.345864000	1.169202000	-2.265816000
1	3.064233000	-0.497251000	-0.871784000
1	2.563189000	-1.367470000	-2.350921000
6	0.379311000	0.038598000	-3.436179000
6	1.002084000	-0.693317000	-4.449380000
1	2.067592000	-0.887731000	-4.428726000
6	0.241997000	-1.167500000	-5.528846000
1	0.729377000	-1.728745000	-6.318588000
6	-1.130101000	-0.897700000	-5.592847000
1	-1.717033000	-1.247610000	-6.434310000
6	-1.741436000	-0.163479000	-4.569086000
1	-2.802234000	0.067666000	-4.624406000
6	-1.001361000	0.308894000	-3.472253000
6	-1.694641000	1.082510000	-2.378997000
1	-1.192611000	2.030513000	-2.167860000
1	-2.728158000	1.299489000	-2.675279000
7	-1.743663000	0.306094000	-1.064380000
6	-2.300637000	-1.081192000	-1.285692000
1	-2.983572000	-1.320994000	-0.463648000
1	-2.875814000	-1.112822000	-2.215602000
6	-1.185953000	-2.096225000	-1.309192000
6	-1.343343000	-3.365507000	-1.866642000
1	-2.266765000	-3.622472000	-2.372993000
6	-0.302919000	-4.294675000	-1.755867000
1	-0.410782000	-5.285188000	-2.183024000
6	0.871988000	-3.931140000	-1.081750000

1	1.691327000	-4.630165000	-0.964655000
6	0.976146000	-2.646813000	-0.549947000
1	1.847738000	-2.305748000	-0.008569000
7	-0.030268000	-1.743981000	-0.678414000
6	-2.485087000	1.099392000	0.009682000
1	-3.515082000	1.325879000	-0.281315000
6	-1.651485000	2.345695000	0.245913000
6	-2.132826000	3.634456000	0.434224000
1	-3.194724000	3.843100000	0.368065000
6	-1.207970000	4.655880000	0.708327000
1	-1.551700000	5.673647000	0.855636000
6	0.154689000	4.347190000	0.793926000
1	0.886733000	5.114192000	1.013492000
6	0.574523000	3.026638000	0.598787000
1	1.607541000	2.720733000	0.678327000
7	-0.319494000	2.053173000	0.323116000
6	-2.393679000	0.279702000	1.284138000
6	-3.384762000	0.122297000	2.244655000
1	-4.371830000	0.542748000	2.090795000
6	-3.065843000	-0.577001000	3.422080000
1	-3.814616000	-0.710047000	4.195038000
6	-1.775518000	-1.094911000	3.590258000
1	-1.498509000	-1.628175000	4.491282000
6	-0.829111000	-0.918901000	2.576141000
1	0.184813000	-1.282084000	2.650824000
7	-1.148670000	-0.246081000	1.450716000
8	1.610087000	-0.069165000	0.810266000
8	1.661587000	0.665053000	2.123531000
1	2.564043000	0.416802000	2.436505000

^{2}5:

26	0.028958850	0.001609873	0.218482875
16	-0.134677441	-0.220229653	2.592128253
6	0.617341470	-1.878948685	3.198341354
6	0.093294494	-2.273631496	4.591160974
6	0.279121530	-1.216650527	5.586291929
7	0.403245402	-0.324322905	6.334582580
1	-0.972000110	-2.532279230	4.539368976
1	0.629054046	-3.180050099	4.905310303
1	0.385681216	-2.656496008	2.468694622
1	1.689273787	-1.673277355	3.205388676
6	-1.932767029	-0.502766761	2.925003074
6	-2.462585157	0.109170552	4.065551612
1	-1.823729295	0.704604938	4.708746895
6	-3.814654897	-0.084558035	4.388554605
1	-4.224881704	0.378056908	5.279079219
6	-4.620520709	-0.884718110	3.570671833
1	-5.659172559	-1.057678095	3.830409210
6	-4.081700901	-1.475479642	2.419395135
1	-4.708296526	-2.097183718	1.785746623
6	-2.731241601	-1.294734906	2.080128634
6	-2.183264447	-1.963703143	0.845766342
1	-2.963817502	-2.585714476	0.388308380
1	-1.330279448	-2.602527928	1.082148721
7	-1.715734409	-0.970685452	-0.208046188
6	-2.789350286	0.051614492	-0.487005491

1	-3.759422154	-0.328040402	-0.155391526
1	-2.847333868	0.213281217	-1.568840373
6	-2.474699664	1.359123556	0.187202467
6	-3.484769260	2.268996517	0.441536691
1	-4.514641200	2.003948561	0.231476291
6	-3.139073288	3.526805250	0.962707943
1	-3.908752047	4.252427657	1.198728707
6	-1.806492742	3.851107691	1.163033685
1	-1.496536996	4.819633228	1.524265779
6	-0.801582320	2.899559560	0.863845321
7	-1.149807039	1.635940108	0.432483520
7	0.545000086	3.197584900	0.917424890
6	1.129471222	4.484762370	0.997421150
6	2.635796794	4.523227764	0.708576509
6	2.947856165	3.810592438	-0.635611128
1	2.811906543	2.723717323	-0.575267490
1	3.993263846	4.004368119	-0.900446836
1	2.318656683	4.211132789	-1.440389602
6	3.085043604	5.994106340	0.604030911
1	4.162404687	6.027680184	0.404433301
1	2.872736528	6.536022817	1.530136651
1	2.560715828	6.503242793	-0.210597872
6	3.383266933	3.825436409	1.874742667
1	3.064427611	2.781646773	1.996844937
1	3.196279901	4.346643569	2.820242523
1	4.461399009	3.849259312	1.675984221
8	0.462173320	5.495893777	1.257754232
1	1.173913959	2.410751431	0.756706743
6	-1.236527831	-1.690821732	-1.467219980
1	-2.028162242	-2.300343915	-1.913311589
6	-0.034949789	-2.508950376	-1.037878458
6	0.310142157	-3.765727945	-1.517139040
1	-0.340960589	-4.285979563	-2.210783205
6	1.518424025	-4.338111961	-1.082944859
1	1.821244804	-5.314196112	-1.444714825
6	2.331393765	-3.629426391	-0.190503721
1	3.270451401	-4.042998179	0.156522478
6	1.925695088	-2.367677069	0.257049158
1	2.515037333	-1.756870642	0.927125260
7	0.757944476	-1.827094131	-0.159085369
6	-0.738198659	-0.600517064	-2.401811828
6	-0.960041012	-0.501169220	-3.770265859
1	-1.551724448	-1.245720315	-4.290502160
6	-0.404034635	0.594799426	-4.454995628
1	-0.571535942	0.710651019	-5.520338554
6	0.357150931	1.538613223	-3.753534954
1	0.798479488	2.387581874	-4.260916349
6	0.538186375	1.381624007	-2.375746395
1	1.104213534	2.079960397	-1.775125851
7	-0.008820884	0.330788957	-1.730109966
8	1.677882417	0.776917670	0.333123080
8	2.485234293	0.301797893	1.523706280
1	3.327615026	0.796148558	1.384457880

^{2}6:

26	0.043626217	0.067232455	-0.105660890

16	1.335845556	0.680958322	-2.071052183
6	2.837965277	-0.479553504	-1.998630599
6	4.078770958	0.130890278	-2.680872442
6	5.198535037	-0.787349250	-2.460521986
7	6.036361269	-1.574874055	-2.236886420
1	3.915367725	0.278994412	-3.755859520
1	4.309299339	1.112354833	-2.248537142
1	3.002732832	-0.610988140	-0.928247953
1	2.541537972	-1.427471608	-2.450687474
6	0.333546914	-0.000700982	-3.475982866
6	0.928563952	-0.737201002	-4.502399329
1	1.992156064	-0.945011252	-4.500048893
6	0.143256853	-1.198345567	-5.569326723
1	0.608346355	-1.763419608	-6.369800816
6	-1.226318123	-0.910865248	-5.607546501
1	-1.833103335	-1.251544512	-6.438735144
6	-1.809348959	-0.170829345	-4.571588486
1	-2.867900032	0.074036759	-4.607162600
6	-1.044182154	0.289701614	-3.487176500
6	-1.709205666	1.074783492	-2.382679520
1	-1.185397262	2.012474555	-2.177612482
1	-2.741404400	1.313950050	-2.667298931
7	-1.755531599	0.298334438	-1.070810029
6	-2.352400859	-1.072445718	-1.285253059
1	-2.999865942	-1.309378663	-0.434275586
1	-2.971965946	-1.079403486	-2.187234284
6	-1.260035118	-2.108360064	-1.371972386
6	-1.447827797	-3.351137708	-1.977381159
1	-2.384508815	-3.574333186	-2.475219512
6	-0.417221035	-4.296617608	-1.929418612
1	-0.547132895	-5.265851765	-2.397353213
6	0.776023481	-3.978525745	-1.264424181
1	1.587504262	-4.693234518	-1.196540195
6	0.908179991	-2.719632586	-0.679582717
1	1.792832040	-2.410858819	-0.139256517
7	-0.086029257	-1.798497989	-0.752834977
6	-2.447021701	1.107309892	0.025239690
1	-3.474813671	1.371944336	-0.240785831
6	-1.566970521	2.324023628	0.253633370
6	-1.998075717	3.628658753	0.457185030
1	-3.052499457	3.876852604	0.412768506
6	-1.032055040	4.615153140	0.715127675
1	-1.335784278	5.644353454	0.870668523
6	0.320567406	4.257661844	0.771474133
1	1.083789519	4.998722413	0.973674737
6	0.687802310	2.923653882	0.565948716
1	1.710727191	2.578742413	0.617232066
7	-0.246074048	1.985155433	0.305445963
6	-2.354533964	0.275880807	1.293614275
6	-3.320885541	0.160547717	2.285295407
1	-4.291843234	0.626531466	2.165020554
6	-2.997305390	-0.557206667	3.450242967
1	-3.725607873	-0.655206284	4.247605685
6	-1.730155772	-1.140427873	3.573170846
1	-1.450452666	-1.693084876	4.461695649
6	-0.809303468	-1.002819611	2.530367650

1	0.189096656	-1.410865911	2.571242894
7	-1.130505509	-0.305579289	1.420710262
8	1.608725455	-0.180005380	0.748497627
8	1.656053341	0.489743222	2.084265894
6	3.043782264	0.351345410	2.669309470
6	3.383220067	-1.128631970	2.830160607
1	4.339183466	-1.231375619	3.355687364
1	3.473506687	-1.616982374	1.854695958
1	2.614600332	-1.636620055	3.424017441
6	4.035761971	1.080512624	1.766668728
1	5.044059653	1.001208849	2.188695807
1	3.778778531	2.143874551	1.689706322
1	4.048479857	0.632897703	0.767618989
6	2.853097629	1.056426820	4.015877273
1	3.814387504	1.081392657	4.541011730
1	2.131043475	0.518621754	4.637839127
1	2.505939636	2.085656260	3.871554721

^{2}7:

26	0.083683900	0.122611887	-0.088486276
16	0.233281512	-0.337842956	2.258283561
6	0.855369172	-1.550554785	5.105915248
6	0.524690551	-2.535811995	4.075067166
1	-0.552966436	-2.739758203	4.108308207
1	1.038729113	-3.483547212	4.286434289
6	0.937801159	-2.074980157	2.664312036
1	0.595854507	-2.786676216	1.911885357
1	2.016384033	-1.928864071	2.580804015
6	-1.532810659	-0.525806491	2.778131858
6	-1.908555768	0.109800774	3.964505942
1	-1.167830362	0.634577643	4.557281426
6	-3.245033665	0.046087606	4.388427306
1	-3.541047517	0.537525578	5.308510301
6	-4.183582899	-0.664391215	3.632121007
1	-5.211955006	-0.736093197	3.969393993
6	-3.794851599	-1.289460419	2.440033450
1	-4.525891666	-1.836965386	1.852270028
6	-2.466706008	-1.222228344	1.989728448
6	-2.100717894	-1.838928074	0.662201764
1	-2.952453615	-2.411890882	0.272599011
1	-1.242760429	-2.506912380	0.744127727
6	-2.804869333	0.291646059	-0.398650755
1	-3.768287334	-0.117895378	-0.082779080
1	-2.909504244	0.653841218	-1.426565234
6	-2.387707425	1.433199603	0.481855940
6	-3.316438313	2.184495063	1.178393080
1	-4.360430495	1.896633494	1.169925175
6	-2.867001484	3.302299479	1.899085048
1	-3.558571594	3.887384286	2.493703535
6	-1.533479564	3.676044984	1.826722004
1	-1.167355808	4.566865788	2.310335182
6	-0.629605642	2.901266940	1.062858925
6	1.064809168	4.676901714	0.750744861
6	2.479616467	4.924420034	0.223607867
6	2.753247766	4.099377226	-1.059378089

1	2.687858600	3.017648513	-0.900935435
1	3.764156086	4.322112574	-1.418380268
1	2.045129147	4.386051606	-1.847655739
6	2.642252342	6.419995846	-0.112306632
1	3.667516361	6.599362079	-0.456542140
1	2.444026690	7.038693275	0.766553044
1	1.948344346	6.723532243	-0.903270069
6	3.455080780	4.551801190	1.371369352
1	3.282333759	3.537830512	1.743837722
1	3.328534115	5.252586493	2.203882258
1	4.488146898	4.624025602	1.010505790
6	-1.458042244	-1.386084289	-1.738744129
1	-2.321727681	-1.926253652	-2.138355120
6	-0.252584304	-2.278964663	-1.534567658
6	-0.038371048	-3.516512735	-2.127961570
1	-0.789299019	-3.949282883	-2.779271134
6	1.166795692	-4.189758950	-1.858752398
1	1.367616172	-5.154269547	-2.311224259
6	2.097697809	-3.604324218	-0.993991686
1	3.030188988	-4.101243019	-0.753574792
6	1.816404135	-2.356988190	-0.429116075
1	2.482895639	-1.838058106	0.238808991
6	-1.027670150	-0.231150134	-2.628478263
6	-1.380200426	-0.026512107	-3.957188039
1	-2.044989826	-0.716702122	-4.464259338
6	-0.854804341	1.097759923	-4.618699702
1	-1.120045911	1.294021526	-5.651529854
6	0.003738847	1.966235074	-3.932651470
1	0.424715630	2.836083667	-4.421627999
6	0.317446738	1.702498536	-2.595852876
1	0.969042940	2.334841903	-2.010264303
7	1.103281720	-0.712480914	5.885508412
7	-1.743963153	-0.778998196	-0.370322368
7	-1.043819871	1.729168972	0.476573711
7	0.666494394	3.316332462	0.813459740
1	1.317838737	2.591897421	0.511776518
7	0.667589923	-1.704342315	-0.704963809
7	-0.198869325	0.624062367	-1.971882627
8	0.308437568	5.592152836	1.111019889
8	1.740446046	0.884085547	-0.110919463
8	2.713045889	0.143217218	0.771838904
6	4.151873841	0.227006375	0.260201039
6	4.195575596	0.009902357	-1.248017305
1	5.234041755	0.098077200	-1.586455339
1	3.602028495	0.770967830	-1.760711007
1	3.821722991	-0.980971154	-1.527653616
6	4.805174092	-0.912094830	1.052631987
1	5.886885371	-0.882060170	0.875655299
1	4.444269867	-1.897728322	0.738992430
1	4.634672023	-0.782457407	2.128058314
6	4.753022454	1.567564735	0.654170937
1	5.831826804	1.545580235	0.456094786
1	4.596452261	1.757876862	1.720155067
1	4.322611172	2.380676929	0.074936969