Supporting Information

for

A High-Spin Square Planar Iron(II)-Siloxide and its Tetrahedral Allogon – Structural and Spectroscopic Models of Fe-Zeolite Sites

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1. General Considerations

Materials: Lithium *tert*-butoxide and iron(II)-chloride were purchased from ABCR. L'H_2 was obtained from a reported procedure by Gunji *et al.* (J. Organomet. Chem., *2011*, **696**, 846–851).

General Procedures: All experimental procedures were carried out at room temperature on a Schlenk line or in a glovebox under an argon or dinitrogen atmosphere. Solvents were purified employing an MBraun Solvent Purification System SPS. Microanalyses were performed on a HEKAtech Euro EA 3000 elemental analyzer. UV/Vis spectra were obtained on a *Varian* Cary 100 UV-visible Spectrophotometer at room temperature using solid samples prepared as KBr pellets.

2. Synthesis of 2

250 mg (0.60 mmol) of L'H_2 were dissolved in THF and 97 mg (1.20 mmol, 2 eq.) of lithium *tert*-butoxide were added. The solution was stirred at room temperature for 3 h. 38 mg (0.30 mmol, 0.5 eq.) of iron(II)-chloride were added and the solution was stirred for another 12 hours slowly changing its colour to blue. All volatiles were removed in vacuo and the resulting blue powder was extracted with diethylether. Diffusion of hexane into a saturated solution of the product in THF resulted in 230 mg (64%) of blue crystals suitable for X-ray analysis. Anal. Calc. for $C_{64}H_{72}FeO_{10}Si_4Li_2$: C, 64.96; H, 6.13; Found: C, 64.78; H, 5.79; ESI-MS: cal.: 880.1298 m/z; Found: 880.1253 m/z, Mössbauer: δ = 0.87 mms^{-1}, ΔE_Q = 0.53 mms^{-1}; UV/vis (0.5 mM in diethylether): 657 nm (81 $L \cdot mol^{-1} \cdot cm^{-1}$).

3. Crystallographic Data

[((Ph)$_2$SiOSi(Ph)$_2$O)$_2$Fe][Li(THF)$_2$]$_2$ (blue crystals)

Empirical formula	$C_{64}H_{72}FeLi_2O_{10}Si_4$
Formular mass	1183.30
Crystal habit, colour	fragment, light blue
Cristal dim. (mm)	0.46 x 0.28 x 0.24
Crystal system	monoclinic
Space Group	Cc
a[Å]	23.0163(7)
b [Å]	14.0910(3)
c[Å]	20.0026(6)
α[°]	90
β[°]	105.909(2)
γ[°]	90
V [Å3]	6238.8(3)
Z	4
D [g.cm^{-1}]	1.260
F(000)	2496
μ(Mo-Kα) [cm^{-1}]	0.374
θ_{range}	3.32- 29.19
Refl. collected	39208
Unique refl.	15812
R_{int}	0.0601
Parameters refined	738
R_1 [I≥2σ (I)]	0.0454
ω_{R2} [I≥2σ (I)]	0.0870
GooF	0.934
Diff. peak/ hole [e/Å3]	-0.29/0.56
CCDC Number	1542038

$[((Ph)_2SiOSi(Ph)_2O)_2Fe][Li(THF)_2]_2$ (pink crystals)

Empirical formula	$C_{64}H_{72}FeLi_2O_{10}Si_4$
Molecular mass	1183.30
Crystal habit, colour	rod, pink
Cristal dim. (mm)	0.42 x 0.24 x 0.18
Crystal system	triclinic
Space group	P-1
a[Å]	12.7108(4)
b [Å]	12.8539(4)
c[Å]	21.7124(7)
α[°]	82.518(2)
β[°]	80.847(2)
γ[°]	62.5150(10)
V [Å3]	3100.44(17)
Z	2
D [$g.cm^{-1}$]	1.268
F(000)	1248
μ(Mo-Kα) [cm^{-1}]	0.377
θ_{range}	2.26- 34.17
Refl. collected	110784
Unique refl.	19392
R_{int}	0.0484
Parameters refined	733
R_1 [I≥2σ (I)]	0.0447
ω_{R2} [I≥2σ (I)]	0.1075
GooF	0.996
Diff. peak/ hole [e/Å3]	-0.52/1.11
CCDC Number	1542039

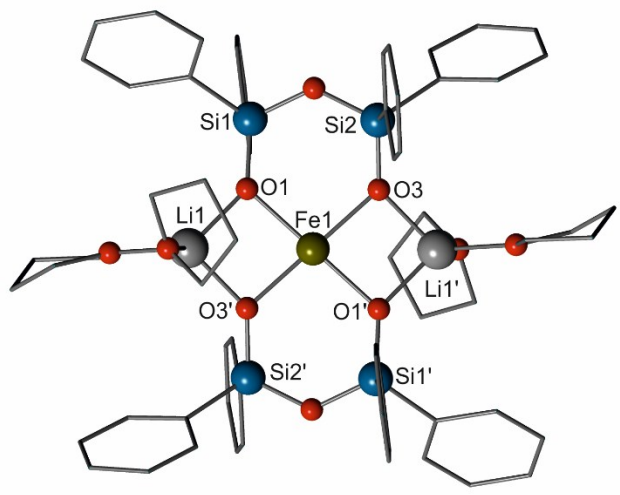

Figure 1 Molecular structure of the pink crystals of ***2****. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–O1 1.9923(11), Fe1–O3 1.9782(10), O1-Fe1-O3 84.38(4), O1-Fe1-O3' 95.62(4), O1-Fe1-O1' 180.0, O3-Fe1-O3' 180.0.*

4. UV/vis-Spectra of 2

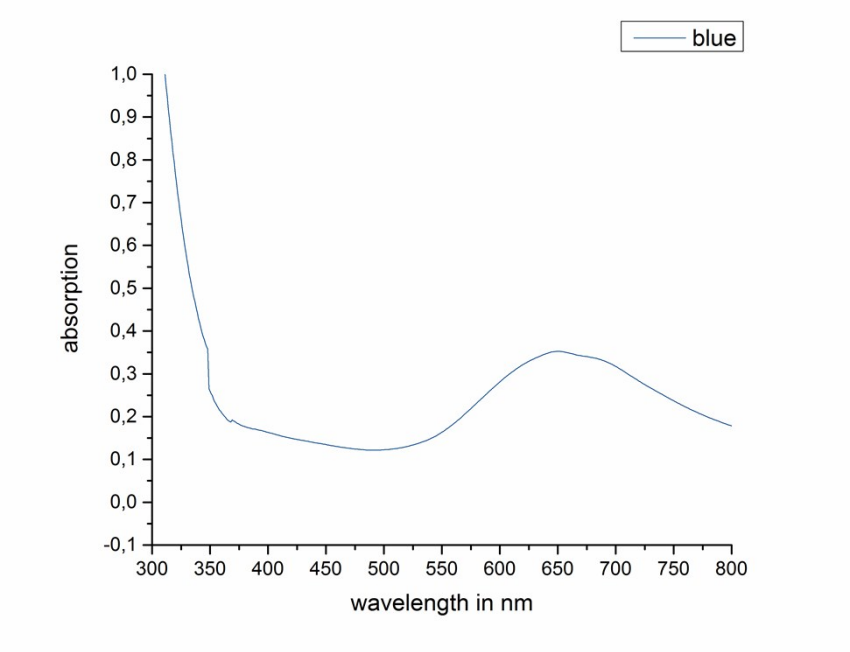

Figure 2 Solid state UV/vis of the blue crystals as KBr pellet.

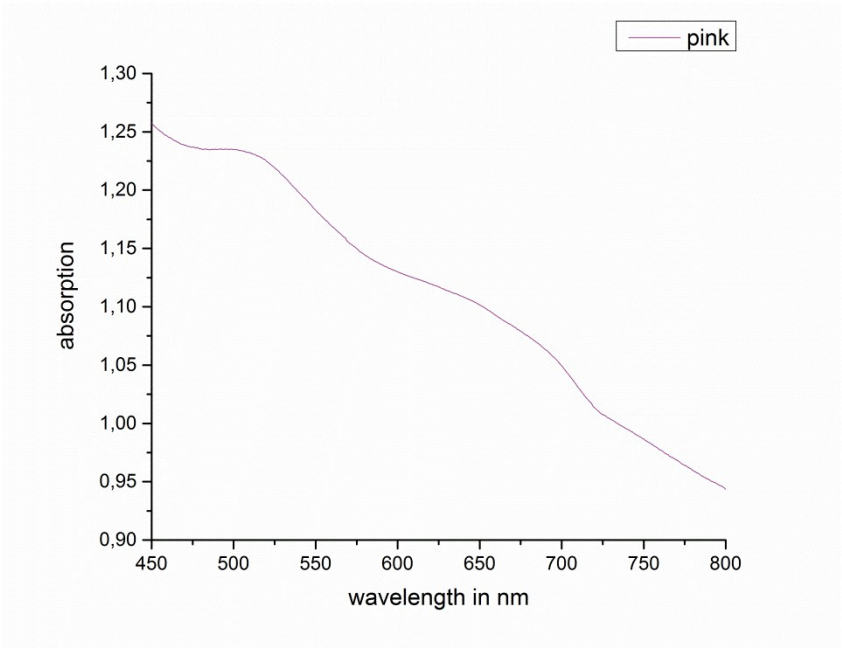

Figure 3 Solid state UV/vis of the pink crystals as KBr pellet.

5. Mössbauer Spectroscopy

Mössbauer spectra were recorded with a Rivertec MCo7.114 source (57Co in Rh matrix) with an activity of about 1 GB using a SeeCo MS6 spectrometer. Spectra were recorded in plastic sample holders with about 30 mg of sample at 13 K and data was accumulated for about 48 hours each. Simulation of the experimental data was performed using the WMOSS4 program ver. F.. Isomeric shifts are referenced to alpha-iron at room temperature.

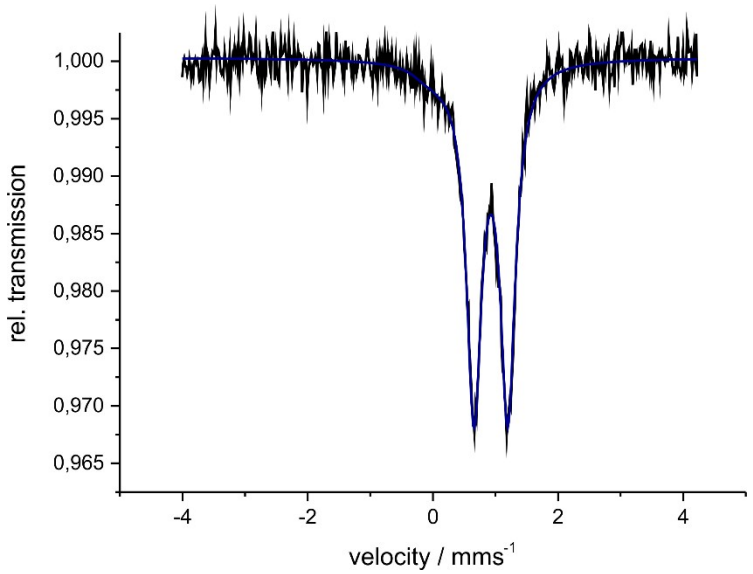

*Figure 4 Mössbauer spectra of blue crystals of **2** at 13 K with black: measured data points and blue: fit.*

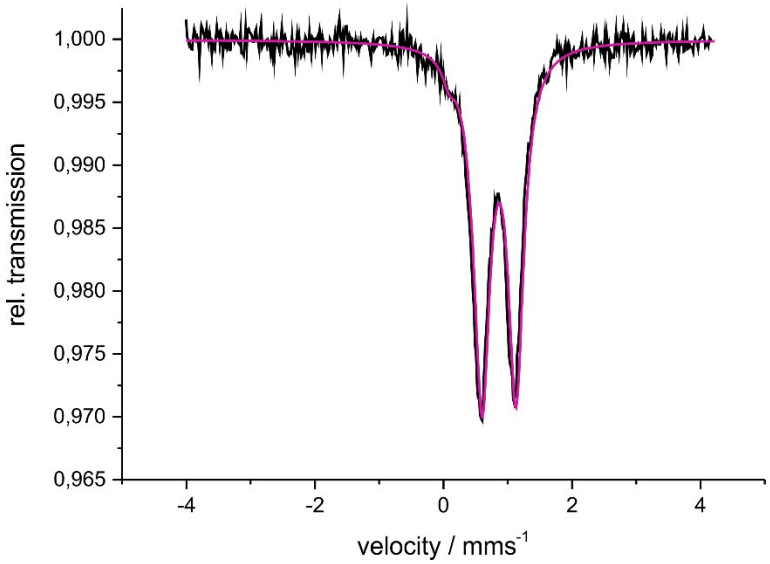

*Figure 5 Mössbauer spectra of pink crystals of **2** at 13 K with black: measured data points and pink: fit.*

6. Density Functional Calculations

Structure optimisations were performed in redundant internal coordinates without symmetry restrictions using the Jaguar 7.8 program package,[1] at the B3LYP[2]/lacv3p**[3] level of theory, accounting for non-covalent (dispersion) interactions with Grimme's *a posteriori* D3 corrections.[4] The molecular structures of the two isomers of $[L'_2Fe][Li(THF)_2]_2$, **2**, as determined by X-ray diffraction analysis were used as starting points. Very tight convergence criteria were chosen for the SCF procedure. Vibrational frequencies for all molecules were computed analytically. Visualization of molecular structures was accomplished with the programs Gauss View (Gaussian, Inc.) and Pymol (Schrodinger, Inc.).

For both isomers the ground state was found to be a quintet state (Table S1, Figure S1, S2), each with four unpaired electrons at the Fe atom (Mulliken atomic spin density: 3.8).

Table 1 Relative electronic energies of different spin states (each at optimised structure).

spin state	relative energy (kJ/mol)	
	distorted tetrahedral	square planar
singlet	272.3	263.3
triplet	71.4	60.9
quintet	0	0

The quintet state of the square planar complex is 14.0 kJ/mol more favourable than the quintet state of the distorted complex.

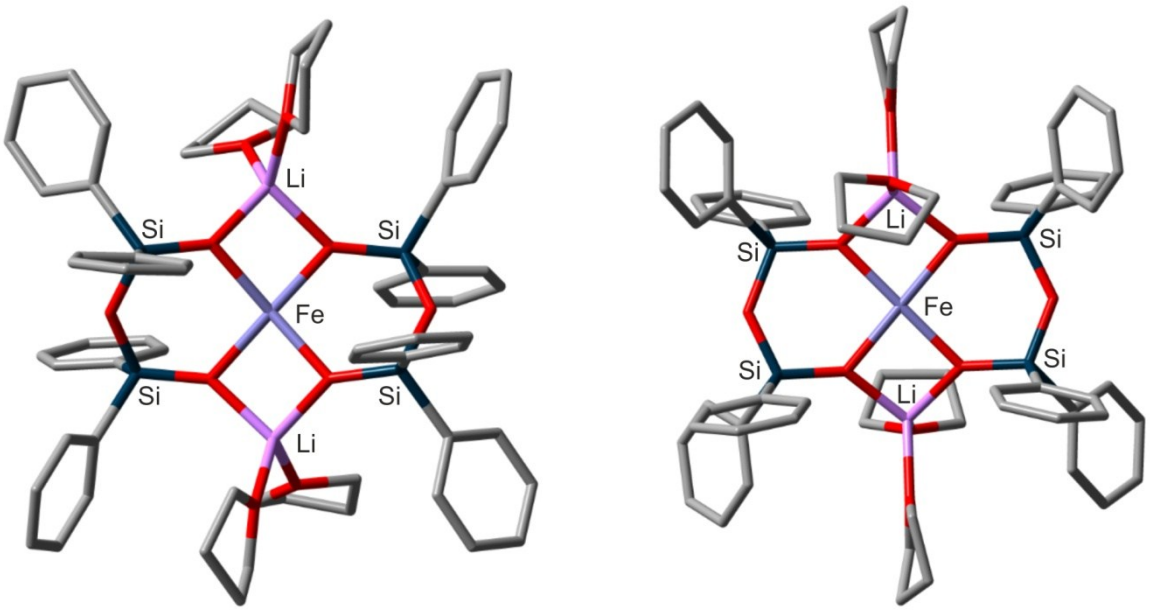

*Figure 6 Optimised molecular structure of the quintet states of the distorted tetrahedral (left) and the square planar (right) isomer of $[L'_2Fe][Li(THF)_2]_2$, **2** (B3LYP-D3/lacv3p**). Hydrogen atoms are omitted for clarity.*

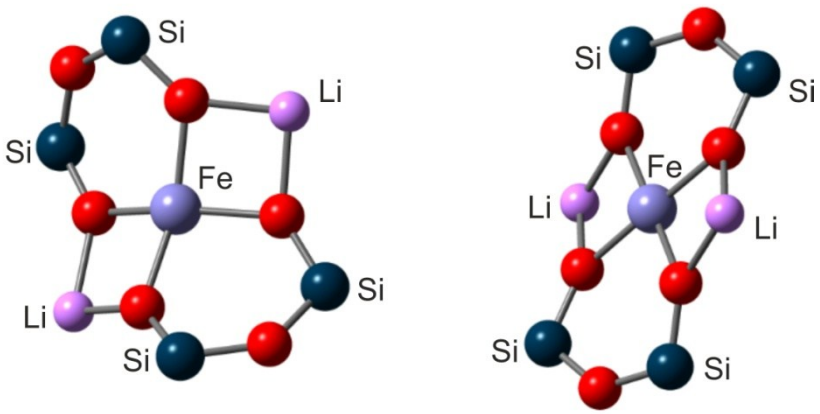

*Figure 7 Optimised molecular structures of the quintet states of the distorted tetrahedral (left) and the square planar (right) isomer of [L'$_2$Fe][Li(THF)$_2$]$_2$, **2** (B3LYP/lacv3p**). Hydrogen atoms, carbon atoms, and the oxygen atoms of THF are omitted for clarity.*

Cartesian coordinates (Å) for the theoretical structure of [L'$_2$Fe][Li(THF)$_2$]$_2$:

B3LYP-D3/lacv3p**, Quintet state

distorted tetrahedral isomer

			z
Fe	0.00000	-0.02260	0.13060
Si	-3.07610	0.45610	-0.75630
Si	-1.79360	2.48860	1.06020
Si	3.12250	-0.41970	-0.69220
Si	1.77910	-2.61350	0.90930
Li	-1.37660	-2.38630	-0.05570
Li	1.30770	2.36460	-0.06970
O	-1.88330	-0.56260	-0.34230
O	-0.35910	1.85210	0.64870
O	1.87070	0.54880	-0.32690
O	0.37720	-1.92490	0.46950
O	-2.19830	-3.06410	1.56840
O	-1.35420	-3.48420	-1.66740
O	1.13180	3.36820	-1.72420
O	2.33010	3.26190	1.29180
O	-3.00990	1.89360	0.08460
O	3.04230	-1.87870	0.10590
C	-1.94750	-2.09850	2.63430
C	-2.88850	0.84460	-2.58890
C	-4.77440	-0.24880	-0.37150
C	-1.77460	4.34120	0.79220
C	-2.19200	1.98970	2.82890
C	3.10120	-0.77650	-2.53910
C	4.75690	0.34690	-0.17570
C	1.77400	-4.41780	0.41810

C	2.08430	-2.34710	2.74390
C	-3.54210	-3.57410	1.67800
C	-0.07620	-3.64320	-2.35040
C	-2.43440	-3.60460	-2.61470
C	-3.20200	-2.09410	3.50610
C	-0.19150	3.77240	-2.17700
C	1.95130	3.00720	-2.85910
C	3.37800	4.23790	1.12180
C	2.63190	2.38340	2.40720
C	-3.62160	1.85720	-3.22360
C	-1.97890	0.10750	-3.36070
C	-5.20100	-1.47150	-0.90940
C	-5.63480	0.41290	0.51610
C	-2.81880	4.99150	0.12250
C	-0.64870	5.09370	1.15980
C	-3.45430	2.18810	3.40570
C	-1.21120	1.35190	3.59990
C	1.93180	-0.55250	-3.27900
C	4.21620	-1.29670	-3.21100
C	5.19610	1.55960	-0.72710
C	5.54980	-0.25280	0.81250
C	2.77740	-4.95720	-0.39660
C	0.66940	-5.22210	0.73890
C	1.66230	-1.14540	3.33020
C	2.79630	-3.25180	3.54130
C	-4.29270	-2.56060	2.53260
C	-0.40520	-3.61190	-3.83790
C	-1.81650	-4.21170	-3.87080
C	-0.07860	3.92770	-3.68920
C	0.99230	2.88690	-4.03840
C	4.22150	4.16020	2.39280
C	4.07930	2.68160	2.78160
C	-3.45540	2.12470	-4.58010
C	-1.82170	0.35890	-4.72260
C	-6.43090	-2.02390	-0.56260
C	-6.86830	-0.13300	0.86560
C	-2.74280	6.35040	-0.17740
C	-0.56900	6.45160	0.86180
C	-3.72590	1.76670	4.70510
C	-1.47630	0.92100	4.89800
C	1.88020	-0.83190	-4.64280
C	4.16680	-1.58800	-4.57200
C	6.38080	2.15740	-0.30490
C	6.73910	0.33870	1.23660
C	2.68200	-6.26040	-0.88200

C	0.57040	-6.52390	0.25550
C	1.95630	-0.84340	4.65630
C	3.08490	-2.96240	4.87440
C	-2.55730	1.37080	-5.33430
C	-7.26630	-1.35580	0.33110
C	-1.61570	7.08220	0.19040
C	-2.73570	1.13180	5.45390
C	2.99640	-1.35440	-5.29130
C	7.15560	1.54580	0.68000
C	1.57610	-7.04400	-0.55880
C	2.67160	-1.75470	5.43220
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H	-1.04160	-2.39630	3.16190
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H	2.90980	5.21080	0.95910
H	3.96700	3.97080	0.23900
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H	1.06110	-0.14140	-2.77750
H	5.13840	-1.47160	-2.66560
H	4.60850	2.04660	-1.49920
H	5.22210	-1.18680	1.25450
H	3.62370	-4.33730	-0.67190
H	-0.13910	-4.81670	1.34000
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H	3.12830	-4.19470	3.11770
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H	0.54730	1.89100	-4.06590
H	1.48570	3.06780	-4.99470
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H	4.27890	2.49160	3.83730
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H	-1.12860	-0.23240	-5.30950
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H	-3.55690	6.83690	-0.70400
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H	6.70320	3.09530	-0.74450
H	7.33790	-0.13990	2.00380
H	3.46380	-6.66160	-1.51810
H	-0.29490	-7.12910	0.50300
H	1.63380	0.10020	5.08300
H	3.63510	-3.67690	5.47720
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H	2.95720	-1.57190	-6.35300
H	8.08000	2.00750	1.00910
H	1.49660	-8.05590	-0.94110
H	2.90270	-1.52600	6.46670
H	-2.83740	-2.60800	-2.82330
H	-3.21700	-4.22080	-2.16640
H	-1.77040	-5.30100	-3.78660
H	-2.37700	-3.95650	-4.77150
H	-0.41930	-2.58290	-4.20410
H	0.32210	-4.16960	-4.42890
H	0.58270	-2.83900	-2.02810
H	0.35410	-4.59800	-2.04240

square planar isomer

	x	**y**	**z**
Fe	0.01160	0.06700	-0.02940
Si	-2.31320	-2.17450	-0.49670
Si	2.41830	2.25950	0.03610

Si	0.33390	-3.13130	0.54640
Si	-0.40310	3.29640	-0.08820
Li	-2.54130	0.95810	0.50090
Li	2.53980	-0.93340	-0.50020
O	-1.84320	-0.67700	-0.08410
O	1.81540	0.82210	-0.42740
O	0.92020	-1.70680	0.03670
O	-0.84380	1.81420	0.41770
O	-3.14620	1.04000	2.38960
O	-4.06580	1.65170	-0.43860
O	3.06740	-1.28550	-2.38290
O	4.14180	-1.44010	0.43430
O	-1.25410	-3.32670	0.07890
O	1.25540	3.44580	-0.07630
C	-2.07120	1.41470	3.27630
C	-3.67780	-0.18500	2.93740
C	-4.25510	1.73050	-1.86960
C	-5.27490	2.08890	0.19790
C	2.64160	-2.54730	-2.93810
C	2.55410	-0.28430	-3.28450
C	4.48140	-1.21870	1.81610
C	5.27840	-2.01950	-0.25090
C	-2.37140	-2.28260	-2.37030
C	-3.98120	-2.55980	0.26710
C	2.95080	2.10680	1.83490
C	3.85180	2.73240	-1.06720
C	1.31130	-4.52590	-0.23510
C	0.43200	-3.19530	2.42040
C	-1.12260	4.60000	1.04180
C	-1.00220	3.49260	-1.86100
C	-1.34390	0.09900	3.55320
C	-2.45840	-0.97180	3.44970
C	-5.39560	2.74520	-2.09820
C	-5.74580	3.24210	-0.67980
C	1.22100	-2.30220	-3.47420
C	1.13570	-0.76040	-3.59950
C	5.96750	-0.89880	1.77860
C	6.47670	-1.87800	0.70690
C	-2.25200	-1.11070	-3.12910
C	-2.50990	-3.49960	-3.05340
C	-5.12320	-1.85460	-0.14150
C	-4.10520	-3.45610	1.33620
C	2.02170	1.59610	2.75640
C	4.24320	2.38890	2.29330
C	4.92170	1.83890	-1.23690

C	3.86170	3.92550	-1.79990
C	0.79810	-5.26010	-1.31170
C	2.63770	-4.76220	0.15690
C	-0.22840	-4.17270	3.17900
C	1.18730	-2.23210	3.10190
C	-0.31700	5.53070	1.70950
C	-2.50270	4.61110	1.29830
C	-1.90480	4.47550	-2.28380
C	-0.59020	2.52890	-2.79540
C	-2.27380	-1.14810	-4.52150
C	-2.51990	-3.54540	-4.44460
C	-6.34380	-2.02410	0.50610
C	-5.32400	-3.62900	1.99000
C	2.37330	1.36250	4.08160
C	4.60450	2.15070	3.61980
C	5.96820	2.12900	-2.10720
C	4.90720	4.21980	-2.67370
C	1.58730	-6.18870	-1.98790
C	3.43010	-5.69030	-0.51340
C	-0.13990	-4.18480	4.56840
C	1.29080	-2.24550	4.49110
C	-0.87150	6.44490	2.60390
C	-3.06130	5.52250	2.18920
C	-2.39140	4.48960	-3.59190
C	-1.07000	2.53790	-4.10080
C	-2.40380	-2.36690	-5.18170
C	-6.44390	-2.90910	1.57930
C	3.67220	1.63190	4.51450
C	5.96140	3.32270	-2.82790
C	2.90620	-6.40180	-1.59250
C	0.62450	-3.22180	5.22700
C	-2.24350	6.44230	2.84440
C	-1.97970	3.51780	-4.50060
H	-2.50030	1.84640	4.18970
H	-1.47090	2.16090	2.76350
H	-4.23310	-0.69010	2.15120
H	-4.36470	0.06900	3.75430
H	-4.50780	0.73730	-2.25230
H	-3.30810	2.04230	-2.30310
H	-5.02050	2.35520	1.22270
H	-6.00160	1.26560	0.21380
H	3.33360	-2.82440	-3.74330
H	2.69530	-3.29510	-2.15130
H	2.60370	0.67260	-2.77250
H	3.18640	-0.25810	-4.18140

H	3.86070	-0.40620	2.18590
H	4.27230	-2.12580	2.39680
H	5.05120	-3.06220	-0.48870
H	5.39860	-1.47100	-1.18540
H	-0.83620	0.09290	4.51840
H	-0.59470	-0.07780	2.78090
H	-2.17170	-1.75280	2.74850
H	-2.66780	-1.44950	4.40790
H	-6.25620	2.25680	-2.56050
H	-5.07730	3.55750	-2.75110
H	-5.17660	4.14280	-0.43840
H	-6.80740	3.46200	-0.55490
H	1.06010	-2.80860	-4.42680
H	0.47130	-2.66810	-2.77580
H	0.44290	-0.37160	-2.85270
H	0.79180	-0.43070	-4.58070
H	6.10660	0.13770	1.46250
H	6.45130	-1.02990	2.74750
H	6.71900	-2.84180	1.16160
H	7.36920	-1.51660	0.19420
H	-2.11810	-0.16390	-2.61960
H	-2.60590	-4.42440	-2.49270
H	-5.05520	-1.15540	-0.96900
H	-3.23200	-4.00970	1.66310
H	1.01330	1.37220	2.42620
H	4.98100	2.78860	1.60520
H	4.92820	0.89890	-0.69400
H	3.03530	4.61930	-1.68890
H	-0.22480	-5.08780	-1.62780
H	3.05910	-4.20490	0.98820
H	-0.82400	-4.93060	2.67980
H	1.67990	-1.45080	2.53640
H	0.75300	5.52650	1.53220
H	-3.14410	3.88920	0.80460
H	-2.23890	5.23410	-1.58350
H	0.10770	1.75690	-2.48940
H	-2.18190	-0.22680	-5.08590
H	-2.61950	-4.49660	-4.95620
H	-7.21650	-1.47000	0.17680
H	-5.40030	-4.32220	2.82070
H	1.63790	0.96700	4.77310
H	5.61350	2.36770	3.95370
H	6.78500	1.42540	-2.22910
H	4.89790	5.14660	-3.23730
H	1.17580	-6.74370	-2.82400

H	4.45360	-5.86190	-0.19680
H	-0.66330	-4.94420	5.13930
H	1.88460	-1.48990	4.99310
H	-0.23330	7.15630	3.11650
H	-4.12970	5.51330	2.37780
H	-3.09150	5.25830	-3.90160
H	-0.73730	1.78260	-4.80410
H	-2.41420	-2.40160	-6.26560
H	-7.39220	-3.04060	2.08860
H	3.95240	1.44480	5.54530
H	6.77370	3.55040	-3.50940
H	3.52220	-7.12280	-2.11840
H	0.69740	-3.23380	6.30910
H	-2.67440	7.15220	3.54190
H	-2.35980	3.52620	-5.51620

7. References

[1] Jaguar, version 7.8; Schrödinger, LLC; New York, NY, 2011.

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