

AM1* parameters for manganese and iron

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Abstract: We report the parameterization of AM1* for the elements manganese and iron. The basis sets for both metals contain one set each of s-, p- and d orbitals. AM1* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Zr, Mo, I and Au. The performance and typical errors of AM1* are discussed for Mn and Fe and compared with available NDDO Hamiltonians.

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Abstract

We report the parameterization of AM1* for the elements manganese and iron. The basis sets for both metals contain one set each of *s*-, *p*- and *d*-orbitals. AM1* parameters are now available for H, C, N, O and F (which use the original AM1 parameters), Al, Si, P, S, Cl, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Zr, Mo, I and Au. The performance and typical errors of AM1* are discussed for Mn and Fe and compared with available NDDO Hamiltonians.

Keywords AM1* · Iron parameters · Manganese parameters · Semiempirical MO-theory

Introduction

We have introduced AM1* [1-7] as an extension of AM1 [8] that uses *d*-orbitals for the elements P, S, Cl, [1] Al, Si, Ti and Zr, [2] Cu and Zn, [3] Br and I, [4] V and Cr, [5] Co and Ni, [6] and Au [7]. The AM1* parameters that are available for molybdenum are a slight modification of Voityuk and Rösch's AM1(d) parameter set [9] to include the AM1* core-core parameters for interactions between Mo and new AM1* elements. The rationalization behind AM1* is to retain the advantages of AM1 (good energies for hydrogen bonds, higher rotation barriers for π-systems than MNDO [10, 11] or PM3 [12-14]) for the first-row elements and improve the performance over AM1 for compounds that contain second-row and heavier elements and to provide a published parameterization for an AM1-like method for the transition metals. As a continuation of this work, we now report AM1* parameters for manganese and iron. Both manganese and iron are important in the chemistry of organometallic and biological catalysts and they play a very important role in biochemical systems especially in the active sites of the enzymes [15, 16].

Theory

AM1* for the two new elements uses the same basic theory as outlined previously. [1, 2] As for other element-H interactions, the core-core repulsion potential for the Mn-H and Fe-H interactions use a distance-dependent term δ_{ij}, rather than the constant term used for core-core potentials for most other interactions in AM1*. [1] This distance-dependent δ_{ij} was also used for the Mo-H and interaction in AM1(d) [9] and for Ti-H, V-H, Cr-H, Co-H, Ni-H, Cu-H, Zn-H, Br-H, Zr-H, Mo-H, I-H and Au-H in AM1* [2-7]. The core-core terms for Mn-H and Fe-H are thus:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 \left[1 + r_{ij}\delta_{ij} \exp\left(-\alpha_{ij} r_{ij}\right)\right] \qquad (1)$$

where all terms have the same meaning as given in reference [1].

The standard MNDO/d formula is used for all other core-core interactions:

$$E^{core}(i-j) = Z_i Z_j \rho_{ss}^0 \left[1 + \delta_{ij} \exp\left(-\alpha_{ij} r_{ij}\right)\right] \qquad (2)$$

The parameterization techniques were those reported in references [1] and [2] and will not be described further here.

Parameterization Data

The target values used for parameterization and their sources are defined in Tables S1, S2 and S3 of the Supplementary Material. We have used heats of formation, Koopmans' theorem ionization potentials, dipole moments and geometrical variables as we did for the Ti, Zr, Cu, Zn, Br, I, V, Cr, Co, Ni and Au parameterizations. [2-7] Because the experimental data for heats of formation of compounds of these two metals are relatively sparse, we have also extended our parameterization data using a small series of model compounds whose heats of formation we have derived from DFT calculations. [17] As before, [1-7] we checked that experimental values for heats of formation were reasonable using DFT calculations.

DFT calculations used the Gaussian 03 suite of programs [18] with the LANL2DZ basis set and standard effective core potentials [19-22] augmented by a set of polarization functions [23] (designated LANL2DZ+pol) and the B3LYP hybrid functional. [24-26]

Experimental parameterization data for manganese and iron were taken largely from the NIST Webbook, [27] but also from the OpenMopac collection [28] and the other experimental and theoretical sources given in the Supplementary Material.

The energetic parameterization data and their sources are given in Table S1 of the Supplementary Material. In addition to the energetic data, geometries, dipole moments and ionization potentials taken from the above sources, crystal structures from the Cambridge Structural Database (CSD) [29] were also used in the parameterization to ensure that not only the energetic and electronic properties for the "prototype" compounds, but also the structures of large manganese and iron compounds are well produced.

Results

Table 1 shows the optimized AM1* parameters. Geometries were optimized with the new AM1* parameterization using VAMP 10.0, [30] while the PM5 calculations used LinMOPAC2.0. [31] Since PM5 was not parameterized for manganese, it was only used for iron compounds. The calculations with PM6 used MOPAC2009. [32] We give related errors for each property, *i.e.*, heats of formation, ionization potentials, dipole moments, geometries as the mean unsigned error (MUE) and mean signed error (MSE). MUE is used to measure the scatter of the calculated results relative to the experimental values, whereas MSE indicates the direction of any systematic deviation of the predictions from experiment.

- *Table 1 about here* -

Manganese

Heats of formation

The calculated heats of formation for our training set of manganese compounds are shown in Table 2. We have compared our results with Stewart's published PM6 method. [33]

- *Table 2 about here* -

AM1* reproduces the heats of formation for the training set of manganese compounds used in parameterization better than PM6. However, we note that this comparison is not strictly valid as it is based on the current parameterization data. As can be seen from Table 2, the AM1* parameterization data set contains 78 compounds, of which 44 are taken from original PM6 parameterization data set. These data convincingly demonstrate the influence of the extent of the training data. AM1* performs significantly better for its extended training set, whereas PM6 performs better for the subset for which it was trained. This situation is unavoidable and is a direct consequence of the relative paucity of data for parameterizing semiempirical MO techniques for transition metals.

Both AM1* and PM6 tend to give positive systematic errors for manganese-containing compounds. For AM1* with a mean signed error (MSE) of 2.3 kcal mol^{-1}, this tendency is less pronounced than for PM6 (MSE of 9.8 kcal mol^{-1}).

The mean unsigned error (MUE) for the AM1* parameterization dataset is 32.3 kcal mol^{-1}, compared with 51.0 kcal mol^{-1} for PM6. PM6 produces especially large errors for the compounds that were not included in its original training set.

The largest errors for AM1* are mainly found for Mn^{3+}, Mn^{2+} and Mn^{+} (-167.3, 161.1 and 95.8 kcal mol^{-1}, respectively). Since the ionization potentials (and hence the heats of formation of the cations) of manganese are important determinants of the reactivity of manganese centers, these errors are important. However, we could not detect serious systematic trends caused by these errors. Molecules that give the largest positive errors for AM1* are MnF_3^- (113.7 kcal mol^{-1}), $MnCl_2O$ (89.5 kcal mol^{-1}), MnF_2^- (79.5 kcal mol^{-1}), $MnCl_2$ (76.5 kcal mol^{-1}), MnF2 (75.8 kcal mol^{-1}), MnC7H5SO4 ($Mn(Cp)(CO)_2(SO_2)$, CPCSMN,) (68.2 kcal mol^{-1}), MnO_2^- (59.1 kcal mol^{-1}), MnH (58.1 kcal mol^{-1}) and MnH^- (55.5 kcal mol^{-1}). The largest negative errors are found for $MnC_7N_2H_{12}S_4^-$ ($Mn(C_3N_2H_4)(C_2H_4S_2)_2^-$, COWHOL) (–141.9 kcal mol^{-1}), *trans*-$Mn(H_2O)_4Cl_2$ (-121.5 kcal mol^{-1}), MnZr (-93.2 kcal mol^{-1}), $MnC_9H_{12}O$ ($Mn(CO)(C_4H_6)_2$, BUTMNC) (-65.5 kcal mol^{-1}), *trans*-$Mn(H_2O)_4Br_2$ (-61.2 kcal mol^{-1}) and MnF_5^- (-60.3 kcal mol^{-1}). AM1* uses the unchanged AM1 parameterization for the elements H, C, N, O and F, which limits the possible accuracy of the parameterization. The large errors with the compounds containing these elements are not surprising as we have pointed out in our previous parameterizations. [3-6] As found for other metals, the large errors in pure AM1* element-containing compounds are likely to be a consequence of our sequential parameterization strategy, in contrast to the simultaneous parameterization used for PM6. [33]

Ionization potentials and dipole moments

A comparison of the calculated and experimental Koopmans' theorem ionization potentials and dipole moments for AM1* and PM6 are given Table 3.

- *Table 3 about here* -

AM1* with an MUE of 1.66 eV performs better than PM6 (MUE of 2.07 eV) for Koopmans' theorem ionization potentials. Both AM1* and PM6 tend to underestimate ionization potentials for manganese-containing compounds. However, this tendency is more serious for PM6 with an MSE of -2.02 eV, compared to the AM1* MSE of -0.77 eV.

Large AM1* errors are found for MnF_2 (-3.06 eV), MnF_3 (-4.00 eV) and MnF_4 (-3.88 eV). This may be an indirect result of using the original AM1 parameters for fluorine. But, however, PM6 also produces very large errors for MnF2 (-2.84 eV), MnF_3 (-4.45 eV) and MnF_4 (-6.59 eV). Since, both methods produce these large errors in the same direction, this may be a result of possible erroneous reference values given in NIST. [27]

AM1* with an MSE of 0.03 Debye shows no significant tendency to systematic errors for dipole moments of manganese compounds, whereas PM6 gives a positive systematic error of 0.14 Debye (MSE). AM1* and PM6 perform comparably, with MUEs of 1.25 and 1.27 Debye, respectively. The largest AM1* errors are found for $MnOF_2$ (4.03 Debye), $MnOI_2$ (3.36 Debye) and MnI (-2.57 Debye). The large error for $MnOF_2$ may be an indirect result of using original AM1 parameters for oxygen and fluorine. However, the large errors for iodine-containing compounds are not surprising and result from the known weakness [4, 5] of the AM1* parameterization in reproducing dipole moments for iodine-containing compounds.

Geometries

Table 4 shows a comparison of AM1* and PM6 results in reproducing the geometries of the manganese-containing compounds.

- Table 4 about here -

Both AM1* and PM6 overestimate bond lengths to manganese systematically by 0.02 and 0.14 Å, respectively. AM1*, with an MUE of 0.13 Å performs better than PM6 (MUE of 0.24 Å) for bond lengths. Here we note that PM6 reproduces bond lengths to be very long for the manganese-transition metal diatomic compounds. Parameterization dataset of PM6 clearly does not cover these model compounds which seriously affects statistics. For the bond angles, PM6 with an MUE of 5.0° performs quite well, compared with AM1* (MUE=12.2°). AM1* and PM6 reproduce bond angles for manganese-containing compounds that are on average 3.0° and 2.1° too small.

Iron

Heats of formation

The results obtained for heats of formation of iron-containing compounds are shown in Table 5. We have compared our results with Stewart's published PM6 method [33] and also the unpublished PM5 method implemented in LinMopac [31].

- Table 5 about here -

AM1* reproduces the heats of formation of the training set of iron compounds used in parameterization better than both PM6 and PM5. Once again, one must consider that this comparison is not strictly valid as it is based on the current parameterization data, which sometimes differ from those used in PM6 and PM5. As can be seen from Table 5, the AM1* parameterization data set contains 98 compounds, of which 55 are taken from the original PM6 parameterization data set. Since PM5 is unpublished, we do not know whether these data cover original PM5 parameterization dataset. These data demonstrate the influence of the extent of the training data. AM1* with the mean unsigned error of 26.5 kcal mol^{-1} performs significantly better for its extended training set than PM6 and PM5 (MUEs of 31.6 and 34.5 kcal mol^{-1}, respectively), whereas PM6 performs better (MUE = 17.8 kcal mol^{-1}) than AM1* and PM5 (MUEs of 32.4 and 33.8 kcal mol^{-1}, respectively) for the subset for which it was trained. As before, we note that, this situation is unavoidable.

AM1* and PM5 underestimate heats of formation for iron compounds by only 3.1 and 5.5 kcal mol^{-1}, respectively. On the other hand, PM6 systematically predicts the heats of formation of iron compounds to be too positive with a mean signed error of 13.7 kcal mol^{-1}. The largest positive errors for AM1* are found for the compounds $FeC_{10}H_{14}O_4$ (bis(acetylacetonate)iron) (100.8 kcal mol^{-1}), $FeC_{36}N_6H_{24}^{2+}$ (ferrous tris(*ortho* phenantholine)) (84.3 kcal mol^{-1}), Fe_2I_4 (72.1 kcal mol^{-1}), Fe^- (68.3 kcal mol^{-1}) and $FeCl_2$ (67.4 kcal mol^{-1}). The largest negative errors for AM1* are found for $Fe(CN)_6^{3-}$ (-217.8 kcal mol^{-1}), $Fe(CN)_6^{4-}$ (−123.3 kcal mol^{-1}), $Fe(H_2O)_5Br^+$ (-73.8 kcal mol^{-1}), $Fe(H_2O)_6^{2+}$ (-69.1 kcal mol^{-1}) and $Fe(H_2O)_5F^+$ (-67.9 kcal mol^{-1}). The large negative errors with oxygen-containing compounds are not surprising as we have pointed out in our previous parameterizations. [5, 6] Generally large errors in AM1* for iron are given by the compounds that contain original AM1 elements or AM1 elements with chlorine, bromine or iodine. We attribute this to a weakness in the

AM1* parameterization for the halogens and also general weakness of the original AM1 parameterization.

Ionization potentials and dipole moments

A comparison of the calculated and experimental ionization potentials and dipole moments of iron-containing compounds for AM1*, PM6 and PM5 are shown in Table 6.

- Table 6 about here -

AM1* and PM5 overestimate Koopmans' theorem ionization potentials of iron-containing compounds with MSEs of 0.42 and 0.52 eV, respectively for the dataset used, whereas PM6 underestimates them by 0.63 eV. AM1* with an MUE of 0.93 eV performs better than both PM5 (MUE=1.03 eV) and PM6 (1.29 eV) for ionization potentials of iron compounds. The large errors for AM1* are mainly found for iron-carbonyl compounds, which is once again an indirect result of using original AM1 parameters for carbon and oxygen.

Both AM1* and PM5 tend to give positive systematic errors for dipole moments of iron-containing compounds with MSEs of 0.31 and 0.34 Debye, respectively, whereas PM6 underestimates by 0.35 Debye. AM1* with an MUE of 0.96 Debye performs slightly better than PM5 (MUE=1.01 Debye) and far better PM6 (1.79 Debye) for dipole moments of iron-containing compounds. The large errors for AM1* are mainly obtained from the compounds containing hydrogen, carbon, oxygen and nitrogen. This is not unexpected because AM1* uses the original AM1 parameters for these elements.

Geometries

The geometrical variables used to parameterize AM1* for iron and a comparison of the AM1*, PM6 and PM5 results are shown in Table 7.

- Table 7 about here -

AM1* shows no systematic error trend for for bond lengths in iron compounds, whereas both PM5 and PM6 overestimate them by 0.08 Å and 0.12 Å, respectively. AM1* with a mean unsigned error of 0.09 Å performs better than PM5 (MUE=0.15 Å) and far better than PM6 (MUE=0.27 Å) for bond lengths. Here once again we note that the large PM6 errors for bond

lengths resulted from iron-transition metal diatomic model compounds and these compounds are not covered by PM6 parameterization dataset.

All three available methods produce negative systematic errors for bond angles of iron-containing compounds. While AM1* underestimates them by 1.3°, PM5 and PM6 also underestimate by 1.7° and 2.6°, respectively. The performance of AM1* for bond angles in iron-containing compounds is comparable to PM5 and better than PM6. The MUEs for AM1* and PM5 are 5.8° and 4.0°, respectively, and for PM6 10.4°. Here the performance of relatively old method PM5 is surprisingly comparable to or better than more modern methods.

Discussion

In this work, we have presented our new AM1* parameters for manganese and iron providing important additional elements for the chemistry of organometallic and biological catalysts and for biochemical systems especially in the active sites of the enzymes. Since the experimental data for the compounds of these two metals are relatively sparse and sometimes of poor quality, we have extended the range of the parameterization dataset and made it more reliable by checking experimental data by including results from DFT calculations. We aim to produce a parameter set that is more robust and generally applicable than the ones trained only using experimental data. For our extended training set used, AM1* parameterizations for manganese and iron give very good energetic and electronic results and also perform very well for the structural properties. Both AM1* and PM6 extend the range of applicability of NDDO-based MNDO-like techniques and provide good starting points for reaction-specific local parameterizations and comparison calculations.

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Supplementary material

The values and the sources of the parameterization data

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Table 1 AM1* parameters for the elements Mn and Fe

Parameter	Mn	Fe
U_{ss} [eV]	-33.2275445	-99.00
U_{pp} [eV]	-27.2535784	-38.200
U_{dd} [eV]	-69.8244104	-83.10
ζ_s [bohr^{-1}]	1.9646322	2.8351398
ζ_p [bohr^{-1}]	18.8965365	37.1808614
ζ_d [bohr^{-1}]	1.2348158	2.2895425
β_s [eV]	-8.1782339	-20.4335137
β_p [eV]	-21.7780791	-66.1689990
β_d [eV]	-6.2336234	-26.5282533
g_{ss} [eV]	5.0059282	8.4047951
g_{pp} [eV]	13.6386827	10.4447975
g_{sp} [eV]	12.3772691	7.6833614
g_{p2} [eV]	96.0815576	13.9440172
h_{sp} [eV]	4.5810741	1.6747978
z_{sn} [bohr^{-1}]	26.0703955	75.1015032
z_{pn} [bohr^{-1}]	1.9830213	0.7086051
z_{dn} [bohr^{-1}]	1.9132012	1.4519328
ρ(core) [bohr^{-1}]	1.2307875	1.0769040
$\Delta H°_f$(atom) [kcal mol^{-1}]	67.701	99.3
F^0_{sd} [eV]	3.3270203	14.1017174
G^2_{sd} [eV]	1.8796412	13.4789419
α(ij)		
H	4.1317380	3.6162132
C	2.8147514	4.0432263
N	1.8883089	3.8755726
O	3.0560315	4.9080254
F	2.5828364	5.3397259
Al	3.5620838	2.0238999
Si	4.2623991	2.6259521
P	2.4072008	2.9339288
S	2.7156160	2.7835642
Cl	2.5923979	2.4937637
Ti	2.3993667	1.4496317
V	3.8190630	1.9484452
Cr	2.7010078	2.0835714
Mn	3.1647134	2.4029678
Fe	2.4029678	3.3225842
Co	2.2792673	2.6623880
Ni	4.5772694	4.4251916
Cu	2.2179615	4.1806484
Zn	4.5907029	4.4519730
Br	3.6890036	2.8134065
Zr	2.6907788	1.7761525
Mo	3.0996586	1.9309316
I	4.1561815	3.5275630
Au	3.0829513	2.8842586
δ(ij)		
H	-12.2571050	-10.2036220
C	3.8500280	41.7471647
N	0.6216587	18.5709816

O	6.1303519	98.7945881
F	1.8592303	98.4859864
Al	32.1147597	4.4417867
Si	79.1063414	7.6467930
P	2.9611118	21.4786698
S	3.7385117	8.4757133
Cl	2.4354976	3.7093945
Ti	1.5477850	1.1499629
V	127.1273363	5.0747072
Cr	7.1369564	3.3205625
Mn	5.9226904	4.7319791
Fe	4.7319791	20.2552175
Co	2.1958330	8.1077071
Ni	265.4707317	178.9982694
Cu	1.8893296	96.7779734
Zn	87.3866849	52.0532649
Br	25.1186833	4.3023002
Zr	3.2445347	2.7554220
Mo	14.0341168	3.2515086
I	53.7439446	43.5771427
Au	10.1393842	7.0870550

Table 2 Calculated AM1* and PM6 heats of formation and errors compared with our target values for the manganese-containing compounds used to parameterize AM1* (all values kcal mol^{-1}). Errors are classified by coloring the boxes in which they appear. Green indicates errors lower than 10 kcal mol^{-1}, yellow 10-20 kcal mol^{-1} and pink those greater than 20 kcal mol^{-1}. The codenames within parentheses indicate the CSD-names of the compounds

Compound	Target $\Delta H°_f$	AM1* $\Delta H°_f$	AM1* Error	PM6 $\Delta H°_f$	PM6 Error
Mn	67.7	67.7	0.0	67.7	0.0
Mn^-	90.2	151.8	61.6	97.9	7.7
Mn^+	239.1	334.9	95.8	224.8	-14.3
Mn^{2+}	599.8	760.9	161.1	566.7	-33.1
Mn^{3+}	1376.0	1208.7	-167.3	1053.2	-322.8
Mn_2	184.3	203.7	19.4	128.2	-56.1
MnH	57.3	115.4	58.1	114.2	56.9
MnH^-	41.2	96.7	55.5	124.2	83.0
MnH_2	114.1	117.0	2.9	114.6	0.5
$Mn(C_5H_5)_2$	66.2	100.8	34.6	95.4	29.2
MnN	123.1	121.1	-2.0	99.2	-23.9
$Mn(NH_3)_6^{2+}$	269.5	275.4	5.9	229.9	-39.6
MnO_2^-	-62.1	-3.0	59.1	-35.3	26.8
MnO_3^-	-127.1	-97.5	29.6	-127.7	-0.6
MnO_4^-	-158.4	-149.7	8.7	-168.8	-10.4
$Mn(H_2O)_6^{2+}$	65.7	9.6	-56.1	50.6	-15.1
$Mn(CO)_3^-$	-54.8	-58.6	-3.8	-113.0	-58.1
$Mn(CO)_4^-$	-122.3	-131.1	-8.7	-157.7	-35.3
$Mn(CO)_5$	-178.0	-152.9	25.1	-174.4	3.6
$Mn(CO)_5H$	-176.8	-180.2	-3.4	-170.4	6.4
$Mn(CO)_6^+$	-49.7	-67.8	-18.1	-78.8	-29.1
$Mn(CO)_5CH_3$	-179.5	-196.5	-17.0	-179.5	0.0
$Mn(CO)_5C_6H_5$	-140.8	-169.9	-29.1	-151.3	-10.5
$Mn(CO)_5(C_6H_5CH_2)$	-151.9	-173.7	-21.8	-154.6	-2.7
$Mn(CO)_5COCH_3$	-215.3	-228.5	-13.2	-230.3	-15.0
$Mn(CO)_5(C_6H_5CO)$	-173.2	-195.1	-21.9	-192.3	-19.1
$MnC_{15}H_{21}O_6$ ($Mn(acac)_3$)	-285.2	-280.0	5.2	-267.2	18.0
$MnC_6H_8O_{10}^-$ (KAMMND)	-543.1	-576.9	-33.8	-537.4	5.7
$MnC_9H_{12}O$ (BUTMNC)	11.9	-53.6	-65.5	22.8	10.9
$MnC_8H_5O_3$ (cyclopentadienyl manganese	-115.2	-65.3	49.9	-81.5	33.7

tricarbonyl)					
$MnC_9H_7O_3$ (HEXMNC)	-95.5	-89.4	6.1	-83.9	11.6
$Mn_2(CO)_9$	-314.5	-310.0	4.5	-323.3	-8.8
$Mn_2(CO)_{10}$	-385.9	-378.7	7.2	-336.8	49.1
Mn(NO)	8.5	47.9	39.4	98.1	89.6
$Mn(CO)(NO)_3$	-60.6	-52.9	7.7	-23.0	37.6
$MnC_{10}N_2H_{12}O_8^-$ (EDTMNK01)	-388.3	-407.0	-18.7	-413.1	-24.8
MnF_2	-126.2	-50.4	75.8	-76.8	49.4
MnF_2^-	-226.0	-146.5	79.5	-106.1	119.9
MnF_3	-188.0	-173.3	14.7	-139.0	49.0
MnF_3^-	-272.2	-158.5	113.7	-164.8	107.4
MnF_4	-231.0	-280.9	-49.9	-170.0	61.0
MnF_4^-	-343.6	-308.5	35.1	-250.3	93.3
MnF_5^-	-373.0	-433.3	-60.3	-300.3	72.7
$Mn_2F_5^-$	-448.3	-440.7	7.6	-257.2	191.1
$Mn_2F_7^-$	-600.0	-630.6	-30.6	-392.6	207.4
$MnOF_2$	-125.8	-120.5	5.3	-114.7	11.1
$Mn(H_2O)_4F_2$ trans	-333.2	-366.8	-33.6	-315.4	17.8
$MnC_7HO_5F_2$ (CDFVMN)	-252.2	-273.1	-20.9	-314.4	-62.2
$Mn(CO)_5CF_3$	-330.5	-355.7	-25.2	-363.7	-33.2
$Mn(CO)_5COCF_3$	-359.7	-378.5	-18.8	-381.9	-22.2
$MnC_7O_7F_3$ (FACMNA)	-437.0	-437.3	-0.3	-431.9	5.1
MnAl	116.5	115.6	-0.9	77.3	-39.2
$MnF_3AlF_4^-$	-704.0	-734.6	-30.6	-220.0	484.0
MnSi	153.2	127.8	-25.4	-275.3	-428.5
MnSiH	93.9	108.2	14.3	-30.9	-124.8
$MnSiH_2$	85.2	91.6	6.4	131.5	46.3
MnP	81.9	81.9	0.0	110.0	28.1
MnPH	67.6	77.4	9.8	82.1	14.5
$MnC_9H_{11}SO_2$ (VALXAI)	-76.7	-109.1	-32.4	-54.7	22.0
$MnC_7H_5SO_4$ (CPCSMN)	-125.0	-56.8	68.2	-119.5	5.5
$MnC_7N_2H_{12}S_4^-$ (COWHOL)	-19.9	-161.8	-141.9	-37.2	-17.3
$MnC_7H_{10}S_2ClO_3$ (GEQLUJ)	-179.2	-198.5	-19.3	-161.0	18.2
MnCl	11.3	69.7	58.4	40.9	29.6
$Mn(CO)_5Cl$ (ZOSWEJ)	-219.5	-240.6	-21.1	-220.0	-0.5
$MnCl_2$	-63.0	13.5	76.5	-31.2	31.8
$Mn(H_2O)_4Cl_2$ trans	-263.1	-384.6	-121.5	-275.3	-12.2
Mn_2Cl_4	-168.2	-163.0	5.2	-30.9	137.3

$MnCl_2O$	-136.0	-46.5	89.5	-67.7	68.3
MnTi	148.8	141.8	-7.1	106.2	-42.6
MnV_2	228.3	228.3	0.0	196.1	-32.2
MnCr	184.4	184.4	0.0	173.3	-11.1
MnCo	158.9	158.8	-0.1	93.3	-65.6
MnNi	80.9	80.9	0.0	168.3	87.4
MnCu	158.2	158.2	0.0	133.6	-24.6
MnZn	89.3	90.4	1.1	-34.3	-123.6
$MnOBr_2$	-37.0	2.5	39.5	-22.2	14.8
$Mn(H_2O)_4Br_2$ trans	-244.3	-305.5	-61.2	-240.4	3.9
$Mn(CO)_5Br$	-210.9	-208.5	2.4	-214.7	-3.8
$MnBr_4^{2-}$ (PYDMNB)	-174.7	-174.4	0.3	-75.9	98.8
MnZr	173.7	80.5	-93.2	190.4	16.7
MnMo	191.5	191.5	0.0	222.7	31.2
MnI	65.8	84.9	19.1	59.1	-6.7
$MnOI_2$	-7.0	37.1	44.1	6.0	13.0
$Mn(H_2O)_4I_2$ trans	-213.7	-267.0	-53.3	-209.7	4.0
$Mn(CO)_5I$ (VUCFAA)	-199.4	-193.5	5.9	-204.2	-4.8
$MnC_{13}N_2H_8O_3I$ (YOMHEN)	-83.2	-68.7	14.5	-80.7	2.5
		AM1*		**PM6**	
N=78					
Most positive error		161.1		484.0	
Most negative error		-167.3		-428.5	
MSE		2.3		9.8	
MUE		32.3		51.0	
RMSD		49.7		95.5	
Results for the PM6 parameterization set (*N=44*)					
MSE		-7.5		0.1	
MUE		31.1		15.8	
RMSD		43.7		20.9	

Table 3 Calculated AM1* and PM6 Koopmans' theorem ionization potentials and dipole moments for manganese-containing compounds. The errors are color coded as follows: green up to 0.5 eV or 0.5 Debye; yellow between 0.5 and 1.0; pink larger than 1.0

Compound	Target	AM1*	Error	PM6	Error
Koopmans' Theorem Ionization Potentials for Manganese Compounds (eV)					
MnH	7.80	9.39	1.59	5.82	-1.98
MnO	8.70	10.58	1.88	7.66	-1.04
$Mn(CO)_5$	8.10	9.18	1.08	7.44	-0.66
$Mn(CO)_5H$	8.85	8.71	-0.14	8.44	-0.41
MnF_2	11.40	8.34	-3.06	8.56	-2.84
MnF_3	12.60	8.60	-4.00	8.15	-4.45
MnF_4	13.50	9.62	-3.88	6.91	-6.59
$MnCl_2$	11.03	9.67	-1.36	8.11	-2.92
$Mn(CO)_5Br$	8.83	8.52	-0.31	8.74	-0.09
$MnBr_2$	10.30	9.70	-0.60	8.78	-1.52
$Mn(CO)_5I$	8.40	8.71	0.31	8.65	0.25
		AM1*		**PM6**	
N=11					
MSE		-0.77		-2.02	
MUE		1.66		2.07	
Dipole Moments for Manganese Compounds (Debye)					
MnH	0.50	0.75	0.25	0.99	0.49
MnN	3.07	4.38	1.31	3.98	0.91
MnNO	5.89	4.46	-1.43	4.45	-1.44
MnO	4.72	4.57	-0.15	3.74	-0.98
MnOH	0.40	1.64	1.24	3.13	2.73
MnF	2.27	0.67	-1.60	4.23	1.96
$MnOF_2$	0.53	4.56	4.03	0.61	0.08
MnAl	1.67	1.60	-0.07	0.19	-1.48
MnSi	3.27	2.85	-0.42	4.03	0.76
MnSiH	3.15	2.75	-0.40	4.03	0.88
$MnSiH_2$	3.22	2.54	-0.68	3.96	0.74
MnP	2.54	2.88	0.34	2.70	0.16
MnPH	4.34	3.12	-1.22	2.97	-1.37
MnS	4.22	3.91	-0.31	1.56	-2.66

MnCl	2.36	0.81	-1.55	3.59	1.23
MnBr	4.29	3.10	-1.19	7.72	3.43
$MnOBr_2$	0.51	2.12	1.61	0.56	0.05
MnI	4.25	1.68	-2.57	2.13	-2.12
$MnOI_2$	0.94	4.30	3.36	0.30	-0.64
		AM1*		**PM6**	
N=19					
MSE		0.03		0.14	
MUE		1.25		1.27	

Table 4 Calculated AM1* and PM6 bond lengths and angles for manganese-containing compounds. The codenames within parentheses indicate the CSD-names of the compounds. The errors are color coded as follows: green up to 0.05 Å or 0.5°; yellow between 0.05-0.1 Å or 0.5-1.0°; pink larger than 0.1 Å or 1°

Compound	Variable	Target	AM1*		PM6	
				Error		Error
Mn_2	Mn-Mn	2.29	2.40	0.11	2.89	0.60
MnH	Mn-H	1.74	1.91	0.18	1.68	-0.05
MnH^-	Mn-H	1.77	1.83	0.06	1.66	-0.11
$Mn(C_5H_5)_2$	Mn-C	2.42	2.79	0.37	2.37	-0.05
MnO_2^-	Mn-O	1.62	1.86	0.24	1.63	0.02
MnO_3^-	Mn-O	1.59	1.85	0.26	1.62	0.03
MnO_4^-	Mn-O	1.64	1.86	0.22	1.63	-0.01
$Mn(H_2O)_6^{2+}$	Mn-O	2.14	2.21	0.07	2.15	0.01
	Mn-O	2.19	2.23	0.04	2.17	-0.02
	Mn-O	2.20	2.27	0.07	2.17	-0.03
$Mn(CH_3)O_3$	Mn=O	1.59	1.84	0.25	1.60	0.01
	Mn-C	1.99	1.91	-0.08	1.93	-0.06
$Mn(CO)_3^-$	Mn-C	1.82	1.97	0.16	1.82	0.01
$Mn(CO)_5$	Mn-C	1.82	1.89	0.07	1.85	0.03
	Mn-C	1.86	1.90	0.04	1.89	0.03
$Mn(CO)_5H$	Mn-C	1.86	1.93	0.07	1.84	-0.02
	Mn-C	1.85	1.92	0.07	1.86	0.01
	H-Mn-C	85.5	90.7	5.2	83.5	-2.0
$Mn(CO)_5CH_3$	Mn-C	1.83	1.90	0.07	1.85	0.02
	Mn-C	1.85	1.94	0.09	1.85	0.00
	Mn-C	2.19	1.99	-0.21	2.08	-0.12
$Mn(CO)_6^+$	Mn-C	1.91	1.95	0.04	1.89	-0.02
$Mn(CO)_5C_6H_5$	Mn-C	1.83	1.90	0.07	1.85	0.02
	Mn-C	1.85	1.94	0.09	1.86	0.01
	Mn-C	2.15	1.99	-0.16	1.99	-0.16
$Mn(CO)_5(C_6H_5CH_2)$	Mn-C	1.82	1.90	0.08	1.85	0.03
	Mn-C	1.85	1.94	0.09	1.85	0.00
	Mn-C	2.26	2.02	-0.24	2.09	-0.17
$Mn(CO)_5COCH_3$	Mn-C	1.84	1.91	0.07	1.85	0.01
	Mn-C	1.85	1.93	0.08	1.88	0.03
	Mn-C	2.17	2.02	-0.15	1.97	-0.20
$Mn(CO)_5(C_6H_5CO)$	Mn-C	1.84	1.90	0.07	1.86	0.02

	Mn-C	1.85	1.93	0.08	1.87	0.02
	Mn-C	2.18	2.03	-0.15	1.97	-0.20
$MnC_6H_8O_{10}^-$ (KAMMND)	Mn-O	1.90	2.07	0.17	1.93	0.03
	Mn-O	2.30	2.28	-0.02	2.44	0.14
	O-Mn-O	91.7	74.1	-17.6	88.3	-3.4
$MnC_9H_{12}O$ (BUTMNC)	Mn-C	1.81	1.92	0.11	1.81	0.00
	Mn-C	2.15	1.98	-0.17	2.11	-0.04
$Mn(CO)_3Cp$ (CPMNCO)	Mn-C(ring)	2.14	2.21	0.07	2.16	0.02
	Mn-C(O)	1.79	1.93	0.14	1.81	0.02
	C-Mn-C	91.4	101.0	9.6	92.6	1.2
$MnC_9H_7O_3$ (HEXMNC)	Mn-C	2.15	2.12	-0.03	2.17	0.02
	Mn-C	1.78	1.92	0.14	1.82	0.04
$Mn_2C_8H_{12}O_8$ ($Mn_2(Ac)_4$)	Mn-Mn	3.31	2.43	-0.88	3.28	-0.03
$Mn_2(CO)_{10}$	Mn-Mn	2.89	2.36	-0.53	2.70	-0.19
$Mn_2(CO)_{10}C_2$ (JIPVOT)	Mn-C	1.86	1.93	0.07	1.84	-0.02
	Mn-C	1.83	1.90	0.07	1.83	0.00
	C-Mn-C	85.9	87.6	1.7	85.4	-0.5
MnN	Mn#N	1.59	1.52	-0.07	1.57	-0.02
MnNO	Mn-N	1.73	1.76	0.03	1.74	0.01
$Mn(NH_3)_6^{2+}$	Mn-N	2.16	2.21	0.05	2.15	-0.01
$Mn(CO)(NO)_3$	Mn-N	1.70	1.67	-0.03	1.64	-0.06
	Mn-C	1.87	1.94	0.06	1.93	0.06
	C-Mn-N	106.0	92.9	-13.1	107.7	1.8
$MnC_{10}N_2H_{12}O_8^-$ (EDTMNK01)	Mn-O	2.02	2.15	0.13	1.95	-0.07
	Mn-O	1.89	2.16	0.27	1.98	0.09
	Mn-N	2.24	2.11	-0.13	2.10	-0.14
	O-Mn-O	88.3	89.7	1.4	84.2	-4.1
	N-Mn-O	77.5	82.2	4.7	83.7	6.2
$MnC_{12}N_2H_{12}O_6$ (XOYHAU)	Mn-O	2.15	2.19	0.04	2.33	0.18
	Mn-N	2.26	1.81	-0.45	1.84	-0.42
	O-Mn-O	85.4	66.7	-18.7	62.5	-22.9
$MnC_{12}N_2H_{16}O_4$ (Mn phenanthroline tetrahydrate)	Mn-O	2.16	2.33	0.17	3.45	1.29
MnF	Mn-F	1.82	2.14	0.32	1.87	0.05
MnF_2	Mn-F	1.79	1.84	0.05	1.78	-0.01
MnF_2^-	Mn-F	1.86	1.88	0.03	1.83	-0.03
$MnOF_2$	Mn-O	1.55	1.89	0.34	1.57	0.02
	Mn-F	1.72	1.79	0.06	1.73	0.01

	O-Mn-F	121.3	102.0	-19.3	124.1	2.8
$Mn(H_2O)_4F_2$ trans	Mn-F	1.98	1.87	-0.11	1.78	-0.20
	Mn-O	2.13	2.35	0.22	2.34	0.21
$MnC_7HO_5F_2$ (CDFVMN)	Mn-C	1.72	1.90	0.18	1.85	0.13
	Mn-C	1.77	1.94	0.17	1.86	0.09
	Mn-C	1.94	2.03	0.09	1.97	0.03
	C-Mn-C	93.8	87.6	-6.2	93.3	-0.5
MnF_3	Mn-F	1.79	1.79	0.00	1.76	-0.03
	F-Mn-F	120.0	141.7	21.7	136.1	16.1
$MnC_7O_7F_3$ (FACMNA)	Mn-C	1.81	1.89	0.08	1.82	0.01
	Mn-O	2.03	2.29	0.26	2.05	0.02
$Mn_2(CO)_8(CF_2)_2$ (DOFPET)	Mn-Mn	2.66	2.42	-0.24	2.73	0.07
	Mn-C(F_2)	2.02	2.10	0.08	1.98	-0.04
	Mn-C(O)	1.88	1.96	0.08	1.87	-0.01
	C-Mn-Mn	49.4	54.8	5.4	46.4	-3.0
MnAl	Mn-Al	2.34	2.34	0.00	2.05	-0.28
$Mn(AlH_2)_2$	Mn-Al	2.41	2.42	0.00	2.15	-0.26
MnSi	Mn-Si	2.34	2.25	-0.10	2.45	0.11
MnSiH	Mn-Si	2.34	2.34	0.00	2.51	0.17
$MnSiH_2$	Mn-Si	2.38	2.44	0.06	2.60	0.22
$MnSi_2C_9H_{15}O_5$ (KIRYUF)	Mn-Si	2.34	2.39	0.05	2.34	0.00
	Mn-O	2.95	2.99	0.04	2.99	0.04
	Si-Mn-Si	71.2	81.5	10.3	68.8	-2.4
MnP	Mn-P	1.97	2.06	0.09	2.15	0.18
MnPH	Mn-P	2.22	2.21	-0.02	2.23	0.01
MnS	Mn-S	1.99	2.14	0.15	2.01	0.02
MnS_2	Mn-S	2.20	2.00	-0.20	2.02	-0.18
$MnC_9H_{11}SO_2$ (VALXAI)	Mn-S	2.27	2.25	-0.02	2.18	-0.09
	Mn-C(O)	1.77	2.01	0.24	1.79	0.02
	Mn-C(C_4)	2.12	2.10	-0.02	2.19	0.07
$MnC_7H_5SO_4$ (CPCSMN)	Mn-S	2.04	2.38	0.34	2.10	0.06
	Mn-C	1.79	1.99	0.20	1.82	0.03
	Mn-C'	2.10	2.10	0.00	2.18	0.08
	S-Mn-C	91.0	80.8	-10.1	92.6	1.6
$MnC_7N_2H_{12}S_4^-$ (COWHOL)	Mn-S	2.32	2.33	0.01	2.28	-0.04
	S-Mn-S	157.5	144.9	-12.6	156.2	-1.3
$MnC_7H_{10}S_2ClO_3$ (GEQLUJ)	Mn-S	2.39	2.35	-0.04	2.26	-0.13
	Mn-C	1.80	1.92	0.12	1.79	-0.01

	Mn-Cl	2.38	2.17	-0.21	2.31	-0.07
	S-Mn-Cl	92.2	87.7	-4.5	88.6	-3.6
$MnC_4N_2H_8S_2O_6$ (WIFSEJ)	Mn-S	2.61	2.26	-0.35	2.21	-0.40
	Mn-O	2.20	2.23	0.03	2.13	-0.07
	O-Mn-S	87.3	111.8	24.5	80.6	-6.7
MnCl	Mn-Cl	2.12	2.31	0.19	2.13	0.01
$Mn(CO)_5Cl$ (ZOSWEJ)	Mn-Cl	2.37	2.13	-0.24	2.23	-0.14
	Mn-C	1.81	1.91	0.10	1.83	0.02
	Mn-C	1.89	1.94	0.05	1.86	-0.03
$Mn(H_2O)_4Cl_2$ trans	Mn-Cl	2.36	2.21	-0.15	1.98	-0.38
	Mn-O	2.10	2.33	0.23	2.21	0.11
	Mn-O	2.50	2.41	-0.09	3.70	1.20
	Mn-O	2.52	2.59	0.07	3.79	1.27
Mn_2Cl_4	Mn-Mn	2.29	2.38	0.09	2.49	0.20
	Mn-Cl	2.13	2.10	-0.03	1.96	-0.18
$MnCl_2O$	Mn-O	1.55	1.89	0.34	1.57	0.02
	Mn-Cl	2.10	2.08	-0.02	1.87	-0.23
	O-Mn-Cl	121.5	86.3	-35.1	119.1	-2.3
$MnC_{12}N_4H_{12}Cl_2O$ (MUPYUR)	Mn-Cl	2.47	2.12	-0.35	2.15	-0.32
	Mn-N(py)	2.26	1.81	-0.45	1.92	-0.34
	Mn-N'	2.34	1.94	-0.40	1.94	-0.40
	N-Mn-N'	95.2	96.2	1.0	94.7	-0.5
MnTi	Mn-Ti	2.25	2.25	0.00	3.62	1.37
MnV_2	Mn-V	2.28	2.21	-0.07	4.90	2.62
MnCr	Mn-Cr	2.35	2.35	0.00	5.90	3.55
MnCo	Mn-Co	2.44	2.27	-0.18	3.39	0.95
MnNi	Mn-Ni	2.50	2.41	-0.08	6.02	3.52
MnCu	Mn-Cu	2.50	2.50	0.00	7.67	5.17
MnZn	Mn-Zn	2.62	2.62	0.00	2.29	-0.33
MnBr	Mn-Br	2.25	2.41	0.16	2.56	0.31
$MnBr_2$	Mn-Br	2.34	2.33	-0.01	2.23	-0.11
$MnOBr_2$	Mn-Br	2.24	2.29	0.05	2.31	0.07
	Mn-O	1.55	1.88	0.33	1.56	0.01
	O-Mn-Br	120.7	104.2	-16.5	125.5	4.8
$Mn(H_2O)_4Br_2$ trans	Mn-Br	2.50	2.40	-0.10	2.45	-0.05
	Mn-O	2.10	2.23	0.13	2.08	-0.02
$Mn(CO)_5Br$	Mn-Br	2.56	2.39	-0.17	2.49	-0.07
	Mn-C	1.82	1.90	0.09	1.82	0.01

	Mn-C'	1.88	1.94	0.07	1.86	-0.01
$MnBr_4^{2-}$ (PYDMNB)	Mn-Br	2.50	2.43	-0.07	2.44	-0.06
$MnAlC_6Br_3O_5$ (CMNCXA10)	Mn-Al	3.53	3.63	0.10	3.45	-0.08
	Mn-C	1.95	1.97	0.02	1.92	-0.03
	Mn-C'	1.87	1.93	0.06	1.87	0.00
	Br-Al-Mn	140.2	117.0	-23.2	126.9	-13.3
MnZr	Mn-Zr	2.43	2.43	0.00	3.02	0.59
MnMo	Mn-Mo	2.27	2.27	0.00	4.71	2.44
MnI	Mn-I	2.46	2.49	0.04	2.29	-0.17
$MnOI_2$	Mn-I	2.45	2.33	-0.12	2.44	-0.01
	Mn-O	1.55	1.89	0.34	1.55	0.00
	O-Mn-I	120.1	112.7	-7.4	116.1	-4.0
$Mn(H_2O)_4I_2$ trans	Mn-I	2.73	2.44	-0.29	2.52	-0.21
	Mn-O	2.08	2.27	0.19	2.24	0.16
$Mn(CO)_5I$ (VUCFAA)	Mn-I	2.69	2.39	-0.30	2.62	-0.07
	Mn-C	1.84	1.91	0.07	1.82	-0.02
$MnC_{13}N_2H_8O_3I$ (YOMHEN)	Mn-I	2.72	2.36	-0.36	2.70	-0.02
	Mn-N	2.05	1.98	-0.07	1.92	-0.13
	Mn-C	1.77	1.93	0.16	1.84	0.07
	I-Mn-N	87.7	87.1	-0.6	83.3	-4.4
$Mn_2(CO)_8I_2$ (SIZYUV)	Mn-Mn	3.98	3.98	0.00	3.96	-0.02
	Mn-I	2.70	2.51	-0.19	2.66	-0.04
	Mn-C	1.88	1.93	0.05	1.85	-0.03
	I-Mn-Mn	42.6	37.8	-4.8	43.6	1.0
MnI(SH)	Mn-I	2.41	2.36	-0.05	2.41	0.00
	Mn-S	2.10	2.27	0.17	2.05	-0.05
	I-Mn-S	115.6	146.2	30.6	101.6	-14.0
$MnI(F)(PH_2)(SH)$	Mn-I	2.50	2.39	-0.12	2.46	-0.04
	Mn-F	1.75	1.79	0.04	1.73	-0.02
	Mn-P	2.27	2.25	-0.02	2.28	0.01
	Mn-S	2.16	2.22	0.06	2.16	0.00
			AM1*		**PM6**	
N=151						
MSE bond length			0.02		0.14	
MUE bond length			0.13		0.24	
N=25						
MSE bond angle			-3.0		-2.1	
MUE bond angle			12.2		5.0	

Table 5 Calculated AM1*, PM6 and PM5 heats of formation and errors compared with our target values for the iron-containing compounds used to parameterize AM1* (all values kcal mol^{-1}). Errors are classified by coloring the boxes in which they appear. Green indicates errors lower than 10 kcal mol^{-1}, yellow 10-20 kcal mol^{-1} and pink those greater than 20 kcal mol^{-1}. The codenames within parentheses indicate the CSD-names of the compounds

Compound	Target	AM1*		PM6		PM5	
	$\Delta H°_f$	$\Delta H°_f$	Error	$\Delta H°_f$	Error	$\Delta H°_f$	Error
Fe	99.3	99.3	0.0	99.3	0.0	99.3	0.0
Fe^+	281.6	251.5	-30.1	262.3	-19.3	282.2	0.6
Fe^-	92.0	160.3	68.3	201.3	109.3	140.7	48.7
Fe^{2+}	654.6	697.5	42.9	637.4	-17.2	647.3	-7.3
Fe^{3+}	1361.0	1361.6	0.6	1358.0	-3.0	1349.7	-11.3
Fe_2	180.0	164.3	-15.7	210.5	30.5	207.5	27.5
FeH	113.9	90.4	-23.5	145.9	32.0	123.7	9.8
FeH^-	91.1	100.4	9.3	193.0	101.9	102.2	11.1
$FeCH_3$	71.0	51.7	-19.3	109.6	38.6	79.9	8.9
FeC_5H_5	88.0	82.5	-5.5	110.7	22.7	142.6	54.6
$Fe(C_5H_5)_2$	57.9	67.2	9.3	49.3	-8.6	102.3	44.3
$Fe(C_5H_5)_2^+$	210.2	250.4	40.2	252.0	41.8	294.3	84.1
FeO	60.0	32.8	-27.2	69.2	9.2	61.0	1.0
FeO^+	265.0	289.8	24.8	246.0	-19.0	259.3	-5.7
FeO^-	31.0	81.7	50.7	94.1	63.1	44.0	13.0
FeO_2^-	-30.0	-26.9	3.1	48.0	78.0	-18.8	11.2
FeOH	32.0	13.5	-18.5	28.5	-3.5	37.6	5.6
$Fe(OH)_2$	-79.0	-83.3	-4.3	-56.5	22.5	-50.4	28.6
$Fe(H_2O)_4(OH)_2$	-294.0	-327.1	-33.1	-334.5	-40.5	-294.5	-0.5
$Fe(H_2O)_5(OH)$	-162.2	-222.7	-60.5	-194.9	-32.7	-183.3	-21.1
$Fe(H_2O)_6^{2+}$	64.8	-4.3	-69.1	90.8	26.0	39.4	-25.4
$Fe(H_2O)_6^{3+}$	492.6	466.0	-26.7	455.0	-37.6	415.8	-76.8
$Fe(CO)_4H_2$	-131.0	-129.8	1.2	-82.7	48.3	-130.9	0.1
Fe(CO)	63.9	26.1	-37.8	59.1	-4.8	60.4	-3.5
$Fe(CO)^-$	34.8	2.0	-32.8	94.1	59.3	42.4	7.6
$Fe(CO)_2$	0.2	6.7	6.5	-3.4	-3.6	1.9	1.7
$Fe(CO)_2^-$	-27.3	-76.6	-49.3	15.9	43.2	-43.8	-16.5
$Fe(CO)_3$	-55.8	-57.3	-1.5	-32.0	23.8	-41.0	14.8
$Fe(CO)_3^-$	-99.2	-124.1	-24.9	-50.2	49.0	-103.6	-4.4
$Fe(CO)_4$	-105.1	-148.7	-43.6	-127.5	-22.4	-108.0	-2.9

$Fe(CO)_4^-$	-160.9	-205.1	-44.2	-139.2	21.7	-173.0	-12.1
$Fe(CO)_4^{2-}$	-115.1	-125.9	-10.8	-114.6	0.5	-127.3	-12.2
$Fe(CO)_5$	-174.0	-181.1	-7.2	-188.4	-14.4	-138.1	35.8
$FeC_6O_{12}^{3-}$ ($Fe(III)(Ox)_3$)	-506.7	-554.5	-47.8	-510.4	-3.7	-618.7	-112.0
$FeC_6H_3O_{12}$ ($H_3Fe(III)(Ox)_3$)	-516.8	-481.2	35.6	-501.4	15.4	-505.4	11.4
$Fe(CO)_4C_2H_4$	-129.2	-142.1	-12.9	-133.4	-4.2	-128.5	0.7
$FeC_8H_2O_6$ (FCPENO)	-173.8	-211.7	-37.9	-170.4	3.4	-210.0	-36.2
$FeC_{10}H_{14}O_4$ (bis(acetylacetonate)iron)	-198.0	-97.2	100.8	-178.2	19.8	-150.6	47.4
$FeC_{15}H_{21}O_6^-$ (Fe(II)(Acac)3 anion)	-340.2	-331.6	8.6	-317.9	22.3	-340.3	-0.1
$Fe_2(CO)_9$	-319.2	-322.7	-3.5	-378.8	-59.6	-324.1	-4.9
$Fe(NH_3)_6^{2+}$	266.4	258.1	-8.3	284.2	17.8	247.0	-19.4
$Fe(CN)_6^{3-}$	374.3	156.5	-217.8	337.0	-37.3	126.8	-247.5
$Fe(CN)_6^{4-}$	484.5	361.2	-123.3	494.5	10.0	318.1	-166.4
$FeC_6N_6H_{24}^{2+}$ ($Fe(II)en)_3$)	283.9	290.6	6.7	286.9	3.0	283.8	-0.1
$FeC_{36}N_6H_{24}^{2+}$ (Ferrous tris(ortho phenantholine)	451.2	535.5	84.3	428.1	-23.1	489.1	37.9
$FeC_8NH_5O_2$ (ACODUR)	-12.1	-12.0	0.1	-9.2	2.9	-5.1	7.0
$FeC_9NH_8O_2^+$ (CPACFE)	113.2	147.1	33.9	96.1	-17.1	145.4	32.2
$Fe(CO)_2(NO)_2$	-75.0	-72.8	2.2	-62.3	12.7	-2.9	72.1
$FeC_{16}N_5H_{11}O_4$	-53.9	8.2	62.1	-54.8	-0.9	-31.2	22.7
$FeC_7NH_5O_5$ (CNOFEA)	-89.2	-57.0	32.2	-94.6	-5.4	-65.6	23.6
$FeC_{10}N_2H_{12}O_8^-$ (Iron(III)EDTA)	-405.6	-377.8	27.9	-404.1	1.5	-425.7	-20.1
FeN	174.3	139.8	-34.5	113.5	-60.8	159.5	-14.8
FeN^+	348.8	340.5	-8.3	294.5	-54.3	326.5	-22.3
FeN^-	123.7	147.8	24.1	162.4	38.7	135.0	11.3
FeF	11.4	44.6	33.2	22.1	10.7	9.9	-1.5
$Fe(H_2O)_5F^+$	-184.7	-252.6	-67.9	-214.0	-29.3	-212.6	-27.9
FeF_2	-93.1	-97.1	-4.0	-80.7	12.4	-95.8	-2.7
FeF_3	-196.2	-159.3	36.9	-162.1	34.1	-185.6	10.6
FeF_6^{3-}	-175.3	-175.3	0.0	-177.2	-1.9	-323.5	-148.2
FeAl	157.8	161.1	3.3	181.0	23.2	181.6	23.8
$Fe(AlH_2)_2$	216.8	214.8	-2.0	299.6	82.8	169.9	-46.9
FeSiH	133.7	121.6	-12.1	190.5	56.8	162.1	28.4
$FeSiH_2$	125.6	122.9	-2.7	184.7	59.1	146.7	21.1
$Fe(SiH_3)_2$	126.7	133.4	6.7	234.7	108.0	136.0	9.3
FeP	156.9	157.0	0.1	29.8	-127.1	174.0	17.1
FePH	104.6	104.4	-0.2	56.8	-47.8	126.3	21.7
FeS	88.6	55.0	-33.6	137.0	48.4	101.1	12.5

$FeC_9H_{10}SO_2$ (CEYTFE)	-59.3	-42.6	16.7	-39.5	19.8	-36.1	23.2
$FeC_{12}H_{14}S_4O_2$ (CIBGAV10)	-73.1	-73.1	0.0	-88.8	-15.7	-64.0	9.1
FeCl	60.0	51.4	-8.6	52.5	-7.5	50.7	-9.3
$FeCl_2$	-33.7	33.7	67.4	12.6	46.3	-24.0	9.7
$FeCl_3$	-60.5	-5.7	54.8	-37.9	22.6	-59.8	0.7
$FeCl_4^{2-}$ (GOXLUA)	-105.2	-106.9	-1.7	-100.8	4.4	-187.2	-82.0
$FeCl_6^{3-}$	-56.5	-109.4	-52.9	-54.3	2.2	-177.8	-121.3
$Fe(H_2O)_5Cl^+$	-148.4	-208.0	-59.6	-146.3	2.1	-175.4	-27.0
$FeC_6N_2H_{18}Cl_3$ (FINJIV)	-91.7	-74.4	17.3	-104.0	-12.3	-126.7	-35.0
FeTi	179.7	179.8	0.1	140.2	-39.5	153.7	-26.0
FeV	146.0	146.0	0.0	250.8	104.8	171.9	25.9
FeCr	215.2	215.2	0.0	216.4	1.2	-20.1	-235.3
FeCo	158.4	158.4	0.0	133.9	-24.5	-11.3	-169.7
FeNi	93.6	93.6	0.0	199.4	105.8	178.5	84.9
FeCu	140.7	140.7	0.0	180.0	39.3	83.8	-56.9
FeZn	119.7	129.6	9.9	113.1	-6.6	180.9	61.2
FeBr	44.7	51.9	7.2	83.7	39.0	58.6	13.9
$FeBr_2$	-9.9	-16.5	-6.6	55.9	65.8	62.3	72.2
Fe_2Br_4	-60.5	-60.5	0.0	-23.5	37.0	-35.2	25.3
$FeC_6H_5BrO_3$ (ALCFEA)	-110.8	-122.7	-11.9	-119.6	-8.8	-132.4	-21.6
$Fe(H_2O)_5Br^+$	-137.9	-211.7	-73.8	-141.7	-3.8	-165.0	-27.1
$Fe(H_2O)_4Br_2$	-248.8	-239.4	9.5	-293.3	-44.5	-281.1	-32.3
FeZr	206.1	180.3	-25.8	311.3	105.2	314.0	107.9
FeMo	251.3	251.2	-0.1	242.5	-8.8	317.4	66.1
$Fe(CO)_3(C_3H_5)I$	-82.1	-86.7	-4.6	-81.0	1.1	-67.1	15.0
$FeC_6H_5IO_3$ (ALCOFE10)	-97.1	-79.1	18.0	-100.2	-3.1	-108.1	-11.0
$Fe(CO)_4I_2$	-151.9	-127.6	24.3	-140.5	11.4	-166.4	-14.5
Fe_2I_4	2.0	74.1	72.1	16.5	14.5	18.8	16.8
FeI_2	21.0	77.7	56.7	125.4	104.4	47.3	26.3
FeI	52.9	91.2	38.3	107.2	54.3	78.3	25.4
FeMn	126.6	126.7	0.1	161.6	35.0	-	-
		AM1*		**PM6**		**PM5**	
N=98							
Most positive error		100.8		109.3		107.9	
Most negative error		-217.8		-127.1		-247.5	
MSE		-3.1		13.7		-5.5	
MUE		26.5		31.6		34.5	
RMSD		41.4		43.6		57.4	

Results for the PM6 parameterization set (*N=55*)			
MSE	-6.3	1.6	-13.5
MUE	32.4	17.8	33.8
RMSD	48.9	23.5	57.6

Table 6 Calculated AM1*, PM6 and PM5 Koopmans' theorem ionization potentials and dipole moments for iron-containing compounds. The errors are color coded as follows: green up to 0.5 eV or 0.5 Debye; yellow between 0.5 and 1.0; pink larger than 1.0

Compound	Target	AM1*	Error	PM6	Error	PM5	Error
Koopmans' Theorem Ionization Potentials for Manganese Compounds (eV)							
$Fe(CO)_4H_2$	9.65	9.36	-0.29	9.70	0.05	9.72	0.07
$Fe(CO)_2$	6.68	8.01	1.33	8.07	1.39	8.51	1.83
$Fe(CO)_4$	8.48	9.90	1.42	9.02	0.54	9.78	1.30
$Fe(CO)_5$	8.60	9.76	1.16	9.23	0.63	9.21	0.61
$FeBr_2$	9.70	10.05	0.35	9.23	-0.47	11.02	1.32
Fe_2Br_4	12.60	11.04	-1.56	7.11	-5.49	10.53	-2.07
$Fe(CO)_4H_2$	9.65	9.46	-0.19	9.70	0.05	9.72	0.07
$FeCl_2$	10.10	11.21	1.11	8.38	-1.72	11.09	0.99
		AM1*		**PM6**		**PM5**	
N=8							
MSE		0.42		-0.63		0.52	
MUE		0.93		1.29		1.03	
Dipole Moments for Manganese Compounds (Debye)							
FeO	7.50	6.62	-0.88	4.44	-3.06	4.95	-2.55
$FeCH_3$	0.90	0.67	-0.23	0.48	-0.42	1.58	0.68
$Fe(CO)_4C_2H_4$	1.50	2.02	0.52	3.25	1.75	1.16	-0.34
FeO_2 (3B1)	2.00	0.91	-1.09	3.33	1.33	0.74	-1.26
FeO_2 (5B2)	3.40	5.06	1.66	2.10	-1.30	4.94	1.54
$Fe(CO)_3C_4H_6$	2.10	0.36	-1.74	4.41	2.31	1.73	-0.37
$FeC_6NH_3O_4$ ($Fe(CO)_4$ acetonitrile)	5.00	7.67	2.67	5.13	0.13	6.61	1.61
FeF	4.19	3.82	-0.37	5.00	0.81	4.53	0.34
FeO_2F_2	1.60	3.04	1.44	2.00	0.40	2.34	0.74
$FeC_{10}PH_{15}O_4$ ($Fe(CO)_4(PEt_3)$	5.20	5.93	0.73	1.56	-3.64	5.10	-0.10
FeCl	4.51	5.98	1.47	1.06	-3.45	4.59	0.08
$FeCl_2O_2$	0.22	0.42	0.20	2.70	2.48	1.65	1.43
FeBr	4.18	4.41	0.23	1.12	-3.06	6.17	1.99
FeI	4.20	3.97	-0.23	5.05	0.85	5.24	1.04
		AM1*		**PM6**		**PM5**	
N=14							
MSE		0.31		-0.35		0.34	
MUE		0.96		1.79		1.01	

Table 7 Calculated AM1*, PM6 and PM5 bond lengths and angles for iron-containing compounds. The codenames within parentheses indicate the CSD-names of the compounds. The errors are color coded as follows: green up to 0.05 Å or 0.5°; yellow between 0.05-0.1 Å or 0.5-1.0°; pink larger than 0.1 Å or 1°

Compound	Variable	Target	AM1*		PM6		PM5	
				Error		Error		Error
Fe_2	Fe-Fe	2.19	2.02	-0.17	2.35	0.17	1.83	-0.36
FeH	Fe-H	1.63	1.63	0.00	1.08	-0.55	1.70	0.07
FeH^-	Fe-H	1.69	1.69	0.00	1.98	0.29	1.70	0.01
FeH^+	Fe-H	1.60	1.53	-0.07	1.16	-0.44	1.58	-0.02
$FeCH_3$	Fe-C	1.97	1.90	-0.07	2.12	0.15	1.94	-0.03
FeC_5H_5	Fe-C	2.17	2.05	-0.13	2.06	-0.11	2.03	-0.14
$Fe(C_5H_5)_2$	Fe-C	2.06	2.12	0.06	2.06	0.00	2.22	0.16
$Fe(III)Cp_2^+$	Fe-C	2.06	1.99	-0.07	2.05	-0.01	2.08	0.02
FeO	Fe-O	1.62	1.76	0.14	1.66	0.04	1.63	0.00
FeO^-	Fe-O	1.69	1.74	0.05	1.79	0.10	1.73	0.04
FeO^+	Fe-O	1.56	1.75	0.19	1.65	0.09	1.65	0.09
FeO_2^-	Fe-O	1.71	1.77	0.06	1.71	0.00	1.72	0.01
FeOH	Fe-O	1.83	1.83	0.00	1.61	-0.22	1.77	-0.06
$Fe(OH)_2$	Fe-O	1.78	1.85	0.08	1.81	0.03	1.79	0.02
$Fe(H_2O)_4(OH)_2$	Fe-O	2.02	1.93	-0.09	1.66	-0.36	1.94	-0.08
	Fe-O	2.08	2.13	0.05	3.17	1.09	2.32	0.24
$Fe(H_2O)_5(OH)$	Fe-O	1.95	1.85	-0.10	1.83	-0.12	1.92	-0.03
	Fe-O	2.05	2.05	0.00	2.17	0.12	2.10	0.05
$Fe(H_2O)_6^{2+}$	Fe-O	2.07	1.99	-0.08	2.01	-0.06	2.15	0.08
	Fe-O	2.15	2.08	-0.07	2.53	0.38	2.22	0.07
$Fe(H_2O)_6^{3+}$	Fe-O	2.06	2.01	-0.05	2.05	-0.01	2.08	0.02
$FeCH_5O_2$ (methyl iron(III)dihydroxide)	Fe-O	1.75	1.83	0.08	1.75	0.00	1.71	-0.04
	Fe-C	1.93	1.92	-0.01	1.64	-0.29	1.93	0.00
Fe(CO)	Fe-C	1.72	1.80	0.08	1.63	-0.09	1.76	0.04
$Fe(CO)^-$	Fe-C	1.79	1.85	0.06	1.80	0.01	1.19	-0.60
$Fe(CO)_2$	Fe-C	1.84	1.88	0.04	1.76	-0.08	1.84	0.00
$Fe(CO)_2^-$	Fe-C	1.79	1.85	0.06	1.75	-0.04	1.82	0.03
$Fe(CO)_3$	Fe-C	1.67	1.82	0.15	1.67	-0.01	1.82	0.14
$Fe(CO)_3^-$	Fe-C	1.82	1.88	0.06	1.40	-0.42	1.92	0.09
$Fe(CO)_4$	Fe-C	1.78	1.89	0.11	1.71	-0.07	1.84	0.05
	Fe-C	1.82	1.89	0.08	1.80	-0.02	1.84	0.02

$Fe(CO)_4^-$	Fe-C	1.78	1.88	0.10	1.66	-0.13	1.84	0.06
$Fe(CO)_4^{2-}$	Fe-C	1.75	1.84	0.09	1.46	-0.29	1.78	0.03
$Fe(CO)_4H_2$	Fe-C	1.81	1.89	0.09	1.81	0.00	1.84	0.03
	Fe-H	1.56	1.58	0.02	1.36	-0.20	1.62	0.06
	H-Fe-C	89.9	89.9	0.0	56.9	-33.0	90.0	0.1
$Fe(CO)_5$	Fe-C(eq)	1.81	1.92	0.11	1.77	-0.04	1.82	0.01
	Fe-C(ax)	1.81	1.92	0.11	1.83	0.02	1.85	0.04
$Fe(CO)_4C_2H_4$	Fe-C	1.81	1.89	0.08	1.75	-0.06	1.84	0.03
	Fe-C	2.13	1.98	-0.15	2.33	0.20	2.00	-0.13
$FeC_6O_{12}^{3-}$ ($Fe(III)(Ox)_3$)	Fe-O	1.97	1.97	0.00	1.99	0.02	2.04	0.07
	O-Fe-O	83.2	80.8	-2.4	99.8	16.6	82.1	-1.1
$FeC_6H_3O_{12}$ ($H_3Fe(III)(Ox)_3$)	Fe-O	1.92	1.93	0.01	1.89	-0.03	2.02	0.10
	Fe-O	2.03	2.02	-0.01	1.98	-0.05	2.22	0.19
$FeC_7H_4O_3$ (cyclobutadiene iron tricarbonyl)	Fe-C(C=O)	1.79	1.92	0.13	1.74	-0.05	1.78	-0.01
	Fe-C(C_4H_4)	2.06	2.00	-0.06	2.08	0.02	2.34	0.28
	C-Fe-C	99.3	83.0	-16.3	88.5	-10.8	97.6	-1.7
$FeC_8H_2O_6$ (FCPENO)	Fe-C	1.81	1.90	0.09	1.82	0.01	1.86	0.05
	Fe-C	2.02	1.95	-0.07	1.83	-0.19	2.02	0.00
$FeC_9H_{12}O$ (BUDFEC01)	Fe-C(O)	1.77	2.05	0.28	1.67	-0.10	1.82	0.05
	Fe-C	2.06	2.05	-0.01	2.08	0.02	2.13	0.07
	C-Fe-C	125.6	117.9	-7.7	109.5	-16.2	118.4	-7.2
$FeC_9H_{12}O$ ($FeCO(1,3\text{-}C_4H_6)_2$)	Fe-C	2.11	2.00	-0.11	2.20	0.09	2.07	-0.04
	C-Fe-C	88.8	83.3	-5.5	79.2	-9.5	82.9	-5.9
$Fe_2(CO)_9$	Fe-C	1.83	1.94	0.11	1.80	-0.03	1.85	0.02
	Fe-C	1.98	1.96	-0.02	2.02	0.04	2.03	0.05
	Fe-C#O	180.0	175.2	-4.8	177.0	-3.0	179.9	-0.1
	Fe-C#O	140.7	138.9	-1.8	141.8	1.1	139.1	-1.7
$FeC_{10}H_{14}O_4$ ($Fe(II)(Acac)_2$)	Fe-O	1.90	1.91	0.01	1.92	0.02	1.94	0.04
	O-Fe-O	93.9	90.9	-3.0	73.4	-20.6	92.4	-1.5
$FeC_{15}H_{21}O_6^-$ ($Fe(II)(Acac)_3$)	Fe-O	1.97	1.98	0.01	2.03	0.06	2.02	0.05
	O-Fe-O	95.1	90.2	-4.9	91.3	-3.7	94.7	-0.4
FeN	Fe-N	1.56	1.72	0.16	1.33	-0.23	1.62	0.06
FeN^+	Fe-N	1.58	1.66	0.08	1.36	-0.22	1.54	-0.04
FeN^-	Fe-N	1.58	1.80	0.22	1.36	-0.22	1.71	0.13
$Fe(NH_3)_6^{2+}$	Fe-N	2.10	2.07	-0.03	2.04	-0.06	2.19	0.09
$Fe(CN)^{4-}$	Fe-C	1.99	1.98	-0.01	1.98	-0.01	1.95	-0.04
	C-Fe-C	180.0	179.9	-0.1	179.9	-0.1	180.0	0.0

$Fe(CO)_2(NO)_2$	Fe-C	1.82	1.97	0.15	1.78	-0.04	1.88	0.05
	Fe-N	1.68	1.79	0.11	1.66	-0.02	1.69	0.01
	C-Fe-C	98.7	83.8	-14.9	90.5	-8.2	86.8	-11.9
	N-Fe-N	109.0	146.7	37.8	92.5	-16.5	118.7	9.7
$FeC_6N_6H_{24}^{2+}$ (Fe(II)en)$_3$)	Fe-N	2.13	2.00	-0.14	2.13	0.00	2.19	0.06
$FeC_7NH_5O_5$ (CNOFEA)	Fe-C	1.79	1.89	0.10	1.93	0.14	1.82	0.03
	Fe-C	2.09	2.06	-0.03	2.07	-0.02	2.27	0.18
	Fe-O	1.97	1.97	0.00	1.84	-0.13	2.06	0.09
$FeC_8NH_5O_2$ (ACODUR)	Fe-C	1.91	1.90	-0.01	1.92	0.01	1.96	0.05
	Fe-C	1.78	1.90	0.12	1.76	-0.02	1.81	0.03
	Fe-C	2.19	2.11	-0.08	2.07	-0.12	2.23	0.04
	C-Fe-C	89.2	83.0	-6.2	74.2	-15.0	89.2	0.0
$FeC_9NH_8O_2^+$ (CPACFE)	Fe-N	1.91	1.95	0.04	1.83	-0.08	2.04	0.13
	Fe-C	1.77	1.91	0.14	1.78	0.01	1.84	0.07
$FeC_{10}N_4H_{10}O_6$ (Diaqua-bis(pyrazinecarboxylato)-iron)	Fe-O	2.11	1.93	-0.18	1.99	-0.12	2.08	-0.03
	Fe-N	2.12	1.95	-0.17	1.92	-0.20	2.08	-0.04
	$Fe\text{-}OH_2$	2.14	2.14	0.00	2.07	-0.07	2.09	-0.05
	O-Fe-N	78.1	83.4	5.3	76.5	-1.6	79.7	1.6
$FeC_{10}N_2H_{12}O_8^-$ (Iron(III)EDTA)	Fe-N	2.03	2.21	0.18	2.19	0.16	2.32	0.29
$FeC_{16}N_5H_{11}O_4$	Fe-O	2.12	2.60	0.48	2.08	-0.04	2.26	0.14
	Fe-O	1.92	1.87	-0.05	1.95	0.03	2.01	0.09
	Fe-N	1.89	1.83	-0.06	1.88	-0.01	2.02	0.13
	O-Fe-O	81.4	78.8	-2.6	73.4	-8.0	77.9	-3.5
$FeC_{17}N_2H_{16}$ (Toluene-(2,2'-bipyridine)-iron)	Fe-N	1.90	1.84	-0.06	1.86	-0.04	1.90	0.00
	Fe-C	2.11	2.07	-0.04	2.07	-0.04	2.28	0.17
	N-Fe-N	81.9	86.3	4.4	76.5	-5.4	82.7	0.8
	N-Fe-C	122.8	114.7	-8.1	107.3	-15.5	128.2	5.4
$FeC_{20}H_{12}N_4$ (iron porphyrin)	Fe-N	1.97	1.93	-0.04	1.92	-0.05	2.02	0.05
$FeC_{36}N_6H_{24}^+$ (ferrous tris(ortophenantholine)	Fe-N	2.05	1.97	-0.08	1.95	-0.10	2.14	0.09
FeF	Fe-F	1.76	1.80	0.04	1.75	-0.01	1.77	0.01
$Fe(II)(H_2O)_5F^+$	Fe-F	1.89	1.70	-0.19	1.82	-0.07	1.90	0.01
	Fe-O	2.05	2.04	-0.01	2.15	0.10	2.10	0.05
FeF_2	Fe-F	1.77	1.71	-0.06	1.76	-0.01	1.79	0.02
FeO_2F_2 (iron(VI)difluoride dioxide)	Fe-F	1.74	1.71	-0.03	1.74	0.00	1.81	0.07
	Fe=O	1.58	1.85	0.27	1.55	-0.03	1.66	0.08
FeF_3	Fe-F	1.78	1.75	-0.03	1.73	-0.05	1.77	-0.01
FeF_6^{3-}	Fe-F	2.06	1.85	-0.21	1.94	-0.12	2.02	-0.04

FeAl	Fe-Al	2.30	2.27	-0.03	2.65	0.35	2.28	-0.03
$Fe(AlH_2)_2$	Fe-Al	2.47	2.39	-0.08	3.06	0.59	2.69	0.22
FeSiH	Fe-Si	2.30	2.30	0.00	3.96	1.66	2.48	0.18
$FeSiH_2$	Fe-Si	2.26	2.31	0.05	4.24	1.98	2.48	0.22
$Fe(SiH_3)_2$	Fe-Si	2.52	2.52	0.00	4.47	1.95	2.52	0.00
FeP	Fe-P	2.23	2.20	-0.03	1.85	-0.38	2.30	0.06
FePH	Fe-P	2.20	2.30	0.10	2.05	-0.15	2.35	0.15
$FeC_{12}P_4H_{34}S_2$ (JIYFAY)	Fe-S	2.35	2.33	-0.02	2.10	-0.25	2.33	-0.02
	Fe-P	2.23	2.64	0.41	2.26	0.03	2.49	0.26
	P-Fe-S	89.4	90.8	1.4	83.1	-6.4	70.5	-18.9
FeS	Fe-S	2.04	2.10	0.06	1.99	-0.05	2.06	0.02
$Fe(SH)_2$	Fe-S	2.25	2.26	0.02	1.82	-0.43	2.26	0.01
$FeC_9H_{10}SO_2$ (CEYTFE)	Fe-S	2.30	2.32	0.02	2.00	-0.30	2.34	0.04
	Fe-C(O)	1.75	1.89	0.14	1.74	-0.01	1.80	0.05
	Fe-C(C_4)	2.12	2.12	0.00	2.04	-0.08	2.25	0.13
	C-Fe-S	90.7	85.0	-5.7	102.3	11.6	91.9	1.2
$FeC_{16}N_2H_{18}S_2O_2$ (dicarbonyl ethylenediamine bis(phenylthiolato)iron)	Fe-S	2.33	2.37	0.04	2.26	-0.07	2.38	0.05
	Fe-S	2.34	2.37	0.03	2.13	-0.21	2.39	0.04
	Fe-N	2.04	1.96	-0.08	2.15	0.11	2.15	0.11
	Fe-N	2.03	1.97	-0.06	1.95	-0.08	2.15	0.12
	Fe-C	1.76	1.88	0.12	1.73	-0.03	1.79	0.03
	N-Fe-S	86.8	88.2	1.4	80.1	-6.7	82.0	-4.8
	C-Fe-S	93.2	84.9	-8.3	96.1	2.9	98.0	4.8
$FeC_9N_3H_{18}S_3O_3$ (tris(N,N-dimethylthiocarbamato)iron(III))	Fe-S	2.43	2.44	0.01	2.49	0.06	2.52	0.09
	Fe-O	2.09	1.99	-0.10	1.88	-0.21	2.07	-0.02
	S-Fe-O	68.9	70.5	1.6	72.1	3.2	66.9	-2.0
	S-Fe-S	103.1	96.0	-7.1	98.0	-5.1	101.5	-1.6
Fe_4S_4	Fe-S	2.27	2.27	0.00	2.28	0.01	2.37	0.10
$FeC_{12}H_{14}S_4O_2$ (CIBGAV10)	Fe-S	2.31	2.35	0.04	2.23	-0.08	2.36	0.05
	Fe-C	1.80	1.89	0.09	1.73	-0.07	1.81	0.01
	S-Fe-S	85.2	85.7	0.4	108.8	23.6	87.8	2.6
	C-Fe-S	90.1	89.4	-0.7	83.1	-7.0	90.7	0.6
$FeC_{14}N_6H_{16}S_6$ (diisothiocyanato-bisthiazoline iron(II))	Fe-N	2.19	2.09	-0.10	1.87	-0.32	2.06	-0.13
	Fe-N(CS)	2.08	1.87	-0.21	1.84	-0.24	1.98	-0.10
	N-Fe-N	73.9	81.3	7.4	101.9	28.0	78.1	4.2
	SCN-Fe-	97.4	94.3	-3.1	99.8	2.4	89.0	-8.4

	NCS							
FeCl	Fe-Cl	2.13	2.23	0.10	1.55	-0.58	2.16	0.02
$Fe(II)(H_2O)_5Cl^+$	Fe-Cl	2.29	2.17	-0.12	2.45	0.16	2.29	0.00
	Fe-O	2.06	2.06	0.00	2.07	0.01	2.10	0.04
$FeCl_2$	Fe-Cl	2.16	2.17	0.01	1.94	-0.22	2.15	-0.01
$FeCl_3$	Fe-Cl	2.16	2.17	0.02	2.18	0.03	2.17	0.02
$FeC_6N_2H_{18}Cl_3$ (FINJIV)	Fe-Cl	2.23	2.35	0.12	2.34	0.11	2.25	0.02
	Fe-N	2.27	1.93	-0.34	1.96	-0.31	2.28	0.01
	Cl-Fe-Cl	121.0	120.1	-0.9	119.4	-1.6	119.8	-1.3
$FeCl_4^-$	Fe-Cl	2.19	2.22	0.03	2.11	-0.08	2.18	-0.01
$FeCl_4^{2-}$ (GOXLUA)	Fe-Cl	2.34	2.33	-0.01	2.35	0.01	2.36	0.02
$FeCl_6^{3-}$	Fe-Cl	2.53	2.54	0.01	2.51	-0.02	2.41	-0.12
FeTi	Fe-Ti	2.54	2.54	0.00	3.67	1.13	-	-
FeV	Fe-V	2.31	2.31	0.00	3.50	1.19	2.04	-0.27
FeCr	Fe-Cr	2.27	2.06	-0.21	3.65	1.38	1.60	-0.67
FeMn	Fe-Mn	2.40	2.40	0.00	5.21	2.81	-	-
FeCo	Fe-Co	2.31	2.30	-0.01	4.68	2.38	1.70	-0.61
FeNi	Fe-Ni	2.33	2.21	-0.12	4.69	2.36	2.05	-0.29
FeCu	Fe-Cu	2.31	2.31	0.00	7.36	5.05	2.05	-0.26
FeZn	Fe-Zn	2.53	2.37	-0.16	2.98	0.45	2.63	0.10
FeBr	Fe-Br	2.23	2.16	-0.07	2.17	-0.06	2.31	0.08
$FeBr_2$	Fe-Br	2.31	2.13	-0.18	2.13	-0.18	2.31	0.00
$FeC_6H_5BrO_3$ (ALCFEA)	Fe-Br	2.50	2.20	-0.30	2.46	-0.04	2.43	-0.07
	Fe-C(C_2)	2.13	2.03	-0.10	2.14	0.01	2.13	0.00
	Fe-C(O)	1.79	1.91	0.12	1.83	0.04	1.85	0.06
	C-Fe-Br	88.6	87.6	-1.0	108.9	20.3	84.9	-3.7
$Fe(H_2O)_5Br^+$	Fe-Br	2.42	2.14	-0.28	2.47	0.05	2.38	-0.04
	Fe-O	2.06	2.10	0.04	2.07	0.01	2.24	0.18
$Fe(H_2O)_4Br_2$	Fe-O	2.07	1.99	-0.08	2.15	0.08	2.09	0.02
	Fe-Br	2.50	2.20	-0.30	2.71	0.21	2.48	-0.02
$FeC_4H_8BrO_7$ (Diaquabromo(oxydiacetato-O,O',O'')-iron(III))	Fe-Br	2.37	2.17	-0.20	2.38	0.01	2.36	-0.02
	Fe-O	2.00	2.07	0.07	1.85	-0.15	1.98	-0.02
	Br-Fe-O	105.6	94.5	-11.1	98.6	-7.0	111.5	5.9
$FeBr_2O_2$	Fe-Br	2.27	2.15	-0.12	2.56	0.29	2.38	0.11
	Fe=O	1.58	1.74	0.16	1.55	-0.03	1.52	-0.06
	Br-Br-Fe	110.6	110.0	-0.6	129.6	19.0	98.1	-12.5
FeZr	Fe-Zr	2.59	2.59	0.00	2.84	0.25	3.04	0.46

FeMo	Fe-Mo	2.21	2.14	-0.07	3.29	1.08	11.58	9.37
FeI	Fe-I	2.44	2.46	0.02	2.70	0.26	2.38	-0.06
$Fe(CO)_3(C_3H_5)I$	Fe-I	2.75	2.61	-0.14	2.80	0.05	2.48	-0.27
	Fe-C(O)	1.80	1.96	0.16	1.73	-0.07	1.84	0.04
	C-Fe-I	81.6	81.7	0.1	75.3	-6.3	76.2	-5.4
$Fe(CO)_3(C_3H_5)I$ (ALCOFE10)	Fe-I	2.75	2.59	-0.16	2.80	0.05	2.59	-0.16
	Fe-C	1.80	1.95	0.15	1.73	-0.07	1.83	0.03
	C-Fe-I	81.6	96.5	14.9	75.3	-6.3	81.8	0.2
FeI_2	Fe-I	2.50	2.49	-0.01	2.55	0.05	2.43	-0.07

	AM1*	PM6	PM5
N=153			
MSE bond length	0.00	0.12	0.08
MUE bond length	0.09	0.27	0.15
N=33			
MSE bond angle	-1.3	-2.6	-1.7
MUE bond angle	5.8	10.4	4.0

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AM1* Parameters for Manganese and Iron

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Supplementary Material

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Table S1: Sources and calculation details for the heats of formation used to parameterize.

Heat of Formation for Manganese Containing Compounds			
Compound	**Target(kcal/mol)**	**Source**	**Total Energy (a.u.)**
Mn	67.7	S1	
Mn^-	90.2	S2	
Mn^+	239.1	S2	
Mn^{2+}	599.8	S2	
Mn^{3+}	1376.0	S2	
Mn_2	184.3	S3	-207.6091449
MnH	57.3	S3	-104.4496606
MnH^-	41.2	S1	
MnH_2	114.1	S3	-104.9516412
$Mn(C_5H_5)_2$	66.2	S1	
MnN	123.1	S3	-158.5358747
$Mn(NH_3)_6^{2+}$	269.5	S4	
MnO_2^-	-62.1	S1	
MnO_3^-	-127.1	S1	
MnO_4^-	-158.4	S1	
$Mn(H_2O)_6^{2+}$	65.7	S4	
$Mn(CO)_3^-$	-54.8	S1	
$Mn(CO)_4^-$	-122.3	S1	
$Mn(CO)_5$	-178.0	S1	
$Mn(CO)_5H$	-176.8	S1	
$Mn(CO)_6^+$	-49.7	S4	
$Mn(CO)_5CH_3$	-179.5	S1	
$Mn(CO)_5C_6H_5$	-140.8	S1	
$Mn(CO)_5(C_6H_5CH_2)$	-151.9	S1	
$Mn(CO)_5COCH_3$	-215.3	S1	
$Mn(CO)_5(C_6H_5CO)$	-173.2	S1	
$MnC_{15}H_{21}O_6$ ($Mn(acac)_3$)	-285.2	S4	
$MnC_6H_8O_{10}^-$ (KAMMND)	-543.1	S4	
$MnC_9H_{12}O$ (BUTMNC)	11.9	S4	
$MnC_8H_5O_3$ (cyclopentadienyl manganese tricarbonyl)	-115.2	S1	
$MnC_9H_7O_3$ (HEXMNC)	-95.5	S4	
$Mn_2(CO)_9$	-314.5	S1	
$Mn_2(CO)_{10}$	-385.9	S5	
Mn(NO)	8.5	S3	-233.8033629
$Mn(CO)(NO)_3$	-60.6	S4	
$MnC_{10}N_2H_{12}O_8^-$ (EDTMNK01)	-388.3	S4	
MnF_2	-126.2	S6	
MnF_2^-	-226.0	S1	
MnF_3	-188.0	S6	
MnF_3^-	-272.2	S1	
MnF_4	-231.0	S6	
MnF_4^-	-343.6	S1	
MnF_5^-	-373.0	S1	
$Mn_2F_5^-$	-448.3	S1	
$Mn_2F_7^-$	-600.0	S1	
$MnOF_2$	-125.8	S4	
$Mn(H_2O)_4F_2$ trans	-333.2	S4	
$MnC_7HO_5F_2$ (CDFVMN)	-252.2	S4	
$Mn(CO)_5CF_3$	-330.5	S1	
$Mn(CO)_5COCF_3$	-359.7	S1	
$MnC_7O_7F_3$ (FACMNA)	-437.0	S4	
MnAl	116.5	S3	-105.8283338

$MnF_3AlF_4^-$	-704.0	S1	
MnSi	153.2	S3	-107.645974
MnSiH	93.9	S3	-108.3333477
$MnSiH_2$	85.2	S3	-108.9445051
MnP	81.9	S3	-110.3663624
MnPH	67.6	S3	-110.9840119
$MnC_9H_{11}SO_2$ (VALXAI)	-76.7	S4	
$MnC_7H_5SO_4$ (CPCSMN)	-125.0	S4	
$MnC_7N_2H_{12}S_4^-$ (COWHOL)	-19.9	S4	
$MnC_7H_{10}S_2ClO_3$ (GEQLUJ)	-179.2	S4	
MnCl	11.3	S6	
$Mn(CO)_5Cl$ (ZOSWEJ)	-219.5	S1	
$MnCl_2$	-63.0	S6	
$Mn(H_2O)_4Cl_2$ trans	-263.1	S4	
Mn_2Cl_4	-168.2	S6	
$MnCl_2O$	-136.0	S3	-209.1453756
MnTi	148.8	S3	-161.8591387
MnV_2	228.3	S3	-246.2697983
MnCr	184.4	S3	-190.0795394
MnCo	158.9	S3	-248.8832029
MnNi	80.9	S3	-273.1382819
MnCu	158.2	S3	-299.9495504
MnZn	89.3	S3	-169.4568054
$MnOBr_2$	-37.0	S4	
$Mn(H_2O)_4Br_2$ trans	-244.3	S4	
$Mn(CO)_5Br$	-210.9	S1	
$MnBr_4^{2-}$ (PYDMNB)	-174.7	S3	-156.9399370
MnZr	173.7	S3	-150.3305742
MnMo	191.5	S3	-171.3221772
MnI	65.8	S3	-115.2527121
$MnOI_2$	-7.0	S4	
$Mn(H_2O)_4I_2$ trans	-213.7	S4	
$Mn(CO)_5I$ (VUCFAA)	-199.4	S1	
$MnC_{13}N_2H_8O_3I$ (YOMHEN)	-83.2	S4	
Heat of Formation for Iron Containing Compounds			
Compound	**Target(kcal/mol)**	**Source**	**Total Energy (a.u.)**
Fe	99.3	S1	
Fe^+	281.6	S2	
Fe^-	92.0	S1	
Fe^{2+}	654.6	S2	
Fe^{3+}	1361.0	S2	
Fe_2	180.0	S7	
FeH	113.9	S6	
FeH^-	91.1	S1	
$FeCH_3$	71.0	S6	
FeC_5H_5	88.0	S1	
$Fe(C_5H_5)_2$	57.9	S1	
$Fe(C_5H_5)_2^+$	210.2	S4	
FeO	60.0	S1	
FeO^+	265.0	S7	
FeO^-	31.0	S1	
FeO_2^-	-30.0	S1	
FeOH	32.0	S7	
$Fe(OH)_2$	-79.0	S1	
$Fe(H_2O)_4(OH)_2$	-294.0	S4	
$Fe(H_2O)_5(OH)$	-162.2	S4	
$Fe(H_2O)_6^{2+}$	64.8	S4	
$Fe(H_2O)_6^{3+}$	492.6	S4	

$Fe(CO)_4H_2$	-131.0	S1	
Fe(CO)	63.9	S6	
$Fe(CO)^-$	34.8	S1	
$Fe(CO)_2$	0.2	S6	
$Fe(CO)_2^-$	-27.3	S1	
$Fe(CO)_3$	-55.8	S6	
$Fe(CO)_3^-$	-99.2	S1	
$Fe(CO)_4$	-105.1	S1	
$Fe(CO)_4^-$	-160.9	S1	
$Fe(CO)_4^{2-}$	-115.1	S4	
$Fe(CO)_5$	-174.0	S1	
$FeC_6O_{12}^{3-}$ ($Fe(III)(Ox)_3$)	-506.7	S4	
$FeC_6H_3O_{12}$ ($H_3Fe(III)(Ox)_3$)	-516.8	S4	
$Fe(CO)_4C_2H_4$	-129.2	S8	
$FeC_8H_2O_6$ (FCPENO)	-173.8	S4	
$FeC_{10}H_{14}O_4$ (bis(acetylacetonate)iron)	-198.0	S6	
$FeC_{15}H_{21}O_6^-$ (Fe(II)(Acac)3 anion)	-340.2	S1	
$Fe_2(CO)_9$	-319.2	S1	
$Fe(NH_3)_6^{2+}$	266.4	S4	
$Fe(CN)_6^{3-}$	374.3	S4	
$Fe(CN)_6^{4-}$	484.5	S4	
$FeC_6N_6H_{24}^{2+}$ ($Fe(II)en)_3$)	283.9	S4	
$FeC_{36}N_6H_{24}^{2+}$ (Ferrous tris(ortho phenantholine)	451.2	S4	
$FeC_8NH_5O_2$ (ACODUR)	-12.1	S4	
$FeC_9NH_8O_2^+$ (CPACFE)	113.2	S4	
$Fe(CO)_2(NO)_2$	-75.0	S4	
$FeC_{16}N_5H_{11}O_4$ (FeN3O2)	-53.9	S4	
$FeC_7NH_5O_5$ (CNOFEA)	-89.2	S4	
$FeC_{10}N_2H_{12}O_8^-$ (Iron(III)EDTA)	-405.6	S4	
FeN	174.3	S3	-178.0254633
FeN^+	348.8	S3	-177.7462654
FeN^-	123.7	S3	-178.1057778
FeF	11.4	S1	
$Fe(H_2O)_5F^+$	-184.7	S4	
FeF_2	-93.1	S1	
FeF_3	-196.2	S1	
FeF_6^{3-}	-175.3	S4	
FeAl	157.8	S3	-125.3330308
$Fe(AlH_2)_2$	216.8	S3	-129.6762622
FeSiH	133.7	S3	-127.8403453
$FeSiH_2$	125.6	S3	-128.4527619
$Fe(SiH_3)_2$	126.7	S3	-134.7832601
FeP	156.9	S3	-129.8171249
FePH	104.6	S3	-130.4956816
FeS	88.6	S1	
$FeC_9H_{10}SO_2$ (CEYTFE)	-59.3	S4	
$FeC_{12}H_{14}S_4O_2$ (CIBGAV10)	-73.1	S4	
FeCl	60.0	S1	
$FeCl_2$	-33.7	S1	
$FeCl_3$	-60.5	S1	
$FeCl_4^{2-}$ (GOXLUA)	-105.2	S4	
$FeCl_6^{3-}$	-56.5	S4	
$Fe(H_2O)_5Cl^+$	-148.4	S4	
$FeC_6N_2H_{18}Cl_3$ (FINJIV)	-91.7	S4	
FeTi	179.7	S3	-181.3805987
FeV	146.0	S3	-194.6316283
FeCr	215.2	S3	-209.601116

FeCo	158.4	S3	-268.4543326
FeNi	93.6	S3	-292.6888573
FeCu	140.7	S3	-319.5481875
FeZn	119.7	S3	-188.9789412
FeBr	44.7	S3	-136.6278006
$FeBr_2$	-9.9	S1	
Fe_2Br_4	-60.5	S1	
$FeC_6H_5BrO_3$ (ALCFEA)	-110.8	S4	
$Fe(H_2O)_5Br^+$	-137.9	S4	
$Fe(H_2O)_4Br_2$	-248.8	S4	
FeZr	206.1	S3	-169.8300106
FeMo	251.3	S3	-190.7974445
$Fe(CO)_3(C_3H_5)I$	-82.1	S1	
$FeC_6H_5IO_3$ (ALCOFE10)	-97.1	S4	
$Fe(CO)_4I_2$	-151.9	S1	
Fe_2I_4	2.0	S1	
FeI_2	21.0	S1	
FeI	52.9	S3	-134.8446233
FeMn	126.6	S3	-258.893132

Table S2: Sources and calculation details for the ionization potentials and dipole moments used to parameterize.

Koopmans' Theorem Ionization Potentials for Manganese Containing Compounds		
Compound	**Target(eV)**	**Source**
MnH	7.80	S1
MnO	8.70	S1
$Mn(CO)_5$	8.10	S1
$Mn(CO)_5H$	8.85	S1
MnF_2	11.40	S1
MnF_3	12.60	S1
MnF_4	13.50	S1
$MnCl_2$	11.03	S1
$Mn(CO)_5Br$	8.83	S1
$MnBr_2$	10.30	S1
$Mn(CO)_5I$	8.40	S1
Koopmans' Theorem Ionization Potentials for Iron Containing Compounds		
$Fe(CO)_4H_2$	9.65	S6
$Fe(CO)_2$	6.68	S6
$Fe(CO)_4$	8.48	S1
$Fe(CO)_5$	8.60	S1
$FeBr_2$	9.70	S1
Fe_2Br_4	12.60	S1
$Fe(CO)_4H_2$	9.65	S1
$FeCl_2$	10.10	S1

Dipole Moments for Manganese Containing Compounds		
Compound	**Target(Debye)**	**Source**
MnH	0.50	S3
MnN	3.07	S3

MnNO	5.89	S3
MnO	4.72	S3
MnOH	0.40	S3
MnF	2.27	S3
$MnOF_2$	0.53	S4
MnAl	1.67	S3
MnSi	3.27	S3
MnSiH	3.15	S3
$MnSiH_2$	3.22	S3
MnP	2.54	S4
MnPH	4.34	S3
MnS	4.22	S4
MnCl	2.36	S3
MnBr	4.29	S4
$MnOBr_2$	0.51	S4
MnI	4.25	S4
$MnOI_2$	0.94	S4
Dipole Moments for Iron Containing Compounds		
FeO	7.50	S6
$FeCH_3$	0.90	S9
$Fe(CO)_4C_2H_4$	1.50	S10
FeO_2 (3B1)	2.00	S11
FeO_2 (5B2)	3.40	S11
$Fe(CO)_3C_4H_6$	2.10	S10
$FeC_6NH_3O_4$ ($Fe(CO)_4$ acetonitrile)	5.00	S10
FeF	4.19	S4
FeO_2F_2	1.60	S4
$FeC_{10}PH_{15}O_4$ ($Fe(CO)_4(PEt_3)$)	5.20	S10
FeCl	4.51	S4
$FeCl_2O_2$	0.22	S4
FeBr	4.18	S4
FeI	4.20	S4

Table S3: Sources and calculation details for the geometrical variables used to parameterize.

Geometrical Variables for Manganese Containing Compounds			
Compound	**Variable**	**Target**	**Source**
Mn_2	Mn-Mn	2.29	S3
MnH	Mn-H	1.74	S3
MnH^-	Mn-H	1.77	S3
$Mn(C_5H_5)_2$	Mn-C	2.42	S3
MnO_2^-	Mn-O	1.62	S3
MnO_3^-	Mn-O	1.59	S3
MnO_4^-	Mn-O	1.64	S4
$Mn(H_2O)_6^{2+}$	Mn-O	2.14	S12
	Mn-O	2.19	S12
	Mn-O	2.20	S12
$Mn(CH_3)O_3$	Mn=O	1.59	S4

	Mn-C	1.99	S4
$Mn(CO)_3^-$	Mn-C	1.82	S3
$Mn(CO)_5$	Mn-C	1.82	S3
	Mn-C	1.86	S3
$Mn(CO)_5H$	Mn-C	1.86	S13
	Mn-C	1.85	S13
	H-Mn-C	85.5	S13
$Mn(CO)_5CH_3$	Mn-C	1.83	S3
	Mn-C	1.85	S3
	Mn-C	2.19	S3
$Mn(CO)_6^+$	Mn-C	1.91	S4
$Mn(CO)_5C_6H_5$	Mn-C	1.83	S3
	Mn-C	1.85	S3
	Mn-C	2.15	S3
$Mn(CO)_5(C_6H_5CH_2)$	Mn-C	1.82	S3
	Mn-C	1.85	S3
	Mn-C	2.26	S3
$Mn(CO)_5COCH_3$	Mn-C	1.84	S3
	Mn-C	1.85	S3
	Mn-C	2.17	S3
$Mn(CO)_5(C_6H_5CO)$	Mn-C	1.84	S3
	Mn-C	1.85	S3
	Mn-C	2.18	S3
$MnC_6H_8O_{10}^-$ (KAMMND)	Mn-O	1.90	S14
	Mn-O	2.30	S14
	O-Mn-O	91.7	S14
$MnC_9H_{12}O$ (BUTMNC)	Mn-C	1.81	S14
	Mn-C	2.15	S14
$Mn(CO)_3Cp$ (CPMNCO)	Mn-C(ring)	2.14	S14
	Mn-C(O)	1.79	S14
	C-Mn-C	91.4	S14
$MnC_9H_7O_3$ (HEXMNC)	Mn-C	2.15	S14
	Mn-C	1.78	S14
$Mn_2C_8H_{12}O_8$ ($Mn_2(Ac)_4$)	Mn-Mn	3.31	S14
$Mn_2(CO)_{10}$	Mn-Mn	2.89	S14
$Mn_2(CO)_{10}C_2$ (JIPVOT)	Mn-C	1.86	S14
	Mn-C	1.83	S14
	C-Mn-C	85.9	S14
MnN	Mn-N	1.59	S3
MnNO	Mn-N	1.73	S3
$Mn(NH_3)_6^{2+}$	Mn-N	2.16	S4
$Mn(CO)(NO)_3$	Mn-N	1.70	S4
	Mn-C	1.87	S4
	C-Mn-N	106.0	S4
$MnC_{10}N_2H_{12}O_8^-$ (EDTMNK01)	Mn-O	2.02	S14
	Mn-O	1.89	S14
	Mn-N	2.24	S14
	O-Mn-O	88.3	S14
	N-Mn-O	77.5	S14
$MnC_{12}N_2H_{12}O_6$ (XOYHAU)	Mn-O	2.15	S14
	Mn-N	2.26	S14
	O-Mn-O	85.4	S14
$MnC_{12}N_2H_{16}O_4$ (Mn	Mn-O	2.16	

phenanthroline tetrahydrate)			S12
MnF	Mn-F	1.82	S3
MnF_2	Mn-F	1.79	S3
MnF_2^-	Mn-F	1.86	S3
$MnOF_2$	Mn-O	1.55	S4
	Mn-F	1.72	S4
	O-Mn-F	121.3	S4
$Mn(H_2O)_4F_2$ trans	Mn-F	1.98	S4
	Mn-O	2.13	S4
$MnC_7HO_5F_2$ (CDFVMN)	Mn-C	1.72	S14
	Mn-C	1.77	S14
	Mn-C	1.94	S14
	C-Mn-C	93.8	S14
MnF_3	Mn-F	1.79	S3
	F-Mn-F	120.0	S3
$MnC_7O_7F_3$ (FACMNA)	Mn-C	1.81	S14
	Mn-O	2.03	S14
$Mn_2(CO)_8(CF_2)_2$ (DOFPET)	Mn-Mn	2.66	S14
	Mn-C(F_2)	2.02	S14
	Mn-C(O)	1.88	S14
	C-Mn-Mn	49.4	S14
MnAl	Mn-Al	2.34	S3
$Mn(AlH_2)_2$	Mn-Al	2.41	S3
MnSi	Mn-Si	2.34	S3
MnSiH	Mn-Si	2.34	S3
$MnSiH_2$	Mn-Si	2.38	S3
$MnSi_2C_9H_{15}O_5$ (KIRYUF)	Mn-Si	2.34	S14
	Mn-O	2.95	S14
	Si-Mn-Si	71.2	S14
MnP	Mn-P	1.97	S4
MnPH	Mn-P	2.22	S3
MnS	Mn-S	1.99	S4
MnS_2	Mn-S	2.20	S3
$MnC_9H_{11}SO_2$ (VALXAI)	Mn-S	2.27	S14
	Mn-C(O)	1.77	S14
	Mn-C(C_4)	2.12	S14
$MnC_7H_5SO_4$ (CPCSMN)	Mn-S	2.04	S14
	Mn-C	1.79	S14
	Mn-C'	2.10	S14
	S-Mn-C	91.0	S14
$MnC_7N_2H_{12}S_4^-$ (COWHOL)	Mn-S	2.32	S14
	S-Mn-S	157.5	S14
$MnC_7H_{10}S_2ClO_3$ (GEQLUJ)	Mn-S	2.39	S14
	Mn-C	1.80	S14
	Mn-Cl	2.38	S14
	S-Mn-Cl	92.2	S14
$MnC_4N_2H_8S_2O_6$ (WIFSEJ)	Mn-S	2.61	S14
	Mn-O	2.20	S14
	O-Mn-S	87.3	S14
MnCl	Mn-Cl	2.12	S4
$Mn(CO)_5Cl$ (ZOSWEJ)	Mn-Cl	2.37	S14
	Mn-C	1.81	S14
	Mn-C	1.89	S14

$Mn(H_2O)_4Cl_2$ trans	Mn-Cl	2.36	S4
	Mn-O	2.10	S4
	Mn-O	2.50	S4
	Mn-O	2.52	S4
Mn_2Cl_4	Mn-Mn	2.29	S4
	Mn-Cl	2.13	S4
$MnCl_2O$	Mn-O	1.55	S4
	Mn-Cl	2.10	S4
	O-Mn-Cl	121.5	S4
$MnC_{12}N_4H_{12}Cl_2O$ (MUPYUR)	Mn-Cl	2.47	S14
	Mn-N(py)	2.26	S14
	Mn-N'	2.34	S14
	N-Mn-N'	95.2	S14
MnTi	Mn-Ti	2.25	S3
MnV_2	Mn-V	2.28	S3
MnCr	Mn-Cr	2.35	S3
MnCo	Mn-Co	2.44	S3
MnNi	Mn-Ni	2.50	S3
MnCu	Mn-Cu	2.50	S3
MnZn	Mn-Zn	2.62	S3
MnBr	Mn-Br	2.25	S4
$MnBr_2$	Mn-Br	2.34	S4
$MnOBr_2$	Mn-Br	2.24	S4
	Mn-O	1.55	S4
	O-Mn-Br	120.7	S4
$Mn(H_2O)_4Br_2$ trans	Mn-Br	2.50	S4
	Mn-O	2.10	S4
$Mn(CO)_5Br$	Mn-Br	2.56	S3
	Mn-C	1.82	S3
	Mn-C'	1.88	S3
$MnBr_4^{2-}$ (PYDMNB)	Mn-Br	2.50	S14
$MnAlC_6Br_3O_5$ (CMNCXA10)	Mn-Al	3.53	S14
	Mn-C	1.95	S14
	Mn-C'	1.87	S14
	Br-Al-Mn	140.2	S14
MnZr	Mn-Zr	2.43	S3
MnMo	Mn-Mo	2.27	S3
MnI	Mn-I	2.46	S4
$MnOI_2$	Mn-I	2.45	S4
	Mn-O	1.55	S4
	O-Mn-I	120.1	S4
$Mn(H_2O)_4I_2$ trans	Mn-I	2.73	S4
	Mn-O	2.08	S4
$Mn(CO)_5I$ (VUCFAA)	Mn-I	2.69	S14
	Mn-C	1.84	S14
$MnC_{13}N_2H_8O_3I$ (YOMHEN)	Mn-I	2.72	S14
	Mn-N	2.05	S14
	Mn-C	1.77	S14
	I-Mn-N	87.7	S14
$Mn_2(CO)_8I_2$ (SIZYUV)	Mn-Mn	3.98	S14
	Mn-I	2.70	S14
	Mn-C	1.88	S14
	I-Mn-Mn	42.6	S14

MnI(SH)	Mn-I	2.41	S4
	Mn-S	2.10	S4
	I-Mn-S	115.6	S4
$MnI(F)(PH_2)(SH)$	Mn-I	2.50	S4
	Mn-F	1.75	S4
	Mn-P	2.27	S4
	Mn-S	2.16	S4
Geometrical Variables for Iron Containing Compounds			
Compound	**Variable**	**Target**	**Source**
Fe_2	Fe-Fe	2.19	S3
FeH	Fe-H	1.63	S4
FeH^-	Fe-H	1.69	S3
FeH^+	Fe-H	1.60	S4
$FeCH_3$	Fe-C	1.97	S3
FeC_5H_5	Fe-C	2.17	S3
$Fe(C_5H_5)_2$	Fe-C	2.06	S4
$Fe(III)Cp_2^+$	Fe-C	2.06	S4
FeO	Fe-O	1.62	S4
FeO^-	Fe-O	1.69	S3
FeO^+	Fe-O	1.56	S3
FeO_2^-	Fe-O	1.71	S3
FeOH	Fe-O	1.83	S4
$Fe(OH)_2$	Fe-O	1.78	S3
$Fe(H_2O)_4(OH)_2$	Fe-O	2.02	S4
	Fe-O	2.08	S4
$Fe(H_2O)_5(OH)$	Fe-O	1.95	S4
	Fe-O	2.05	S4
$Fe(H_2O)_6^{2+}$	Fe-O	2.07	S4
	Fe-O	2.15	S4
$Fe(H_2O)_6^{3+}$	Fe-O	2.06	S12
$FeCH_5O_2$ (methyl iron(III)dihydroxide)	Fe-O	1.75	S4
	Fe-C	1.93	S4
Fe(CO)	Fe-C	1.72	S3
$Fe(CO)^-$	Fe-C	1.79	S3
$Fe(CO)_2$	Fe-C	1.84	S3
$Fe(CO)_2^-$	Fe-C	1.79	S3
$Fe(CO)_3$	Fe-C	1.67	S3
$Fe(CO)_3^-$	Fe-C	1.82	S3
$Fe(CO)_4$	Fe-C	1.78	S3
	Fe-C	1.82	S3
$Fe(CO)_4^-$	Fe-C	1.78	S3
$Fe(CO)_4^{2-}$	Fe-C	1.75	S4
$Fe(CO)_4H_2$	Fe-C	1.81	S15
	Fe-H	1.56	S15
	H-Fe-C	89.9	S15
$Fe(CO)_5$	Fe-C(eq)	1.81	S4
	Fe-C(ax)	1.81	S4
$Fe(CO)_4C_2H_4$	Fe-C	1.81	S4
	Fe-C	2.13	S4
$FeC_6O_{12}^{3-}$ ($Fe(III)(Ox)_3$)	Fe-O	1.97	S4
	O-Fe-O	83.2	S4
$FeC_6H_3O_{12}$ ($H_3Fe(III)(Ox)_3$)	Fe-O	1.92	S4
	Fe-O	2.03	S4

$FeC_7H_4O_3$ (cyclobutadiene iron tricarbonyl)	Fe-C(C=O)	1.79	S4
	Fe-C(C_4H_4)	2.06	S4
	C-Fe-C	99.3	S4
$FeC_8H_2O_6$ (FCPENO)	Fe-C	1.81	S14
	Fe-C	2.02	S14
$FeC_9H_{12}O$ (BUDFEC01)	Fe-C(O)	1.77	S14
	Fe-C	2.06	S14
	C-Fe-C	125.6	S1
$FeC_9H_{12}O$ ($FeCO(1,3\text{-}C_4H_6)_2$)	Fe-C	2.11	S4
	C-Fe-C	88.8	S4
$Fe_2(CO)_9$	Fe-C	1.83	S16
	Fe-C	1.98	S16
	Fe-C#O	180.0	S16
	Fe-C#O	140.7	S16
$FeC_{10}H_{14}O_4$ ($Fe(II)(Acac)_2$)	Fe-O	1.90	S4
	O-Fe-O	93.9	S4
$FeC_{15}H_{21}O_6^-$ ($Fe(II)(Acac)_3$)	Fe-O	1.97	S4
	O-Fe-O	95.1	S4
FeN	Fe-N	1.56	S3
FeN^+	Fe-N	1.58	S3
FeN^-	Fe-N	1.58	S3
$Fe(NH_3)_6^{2+}$	Fe-N	2.10	S4
$Fe(CN)_6^{4-}$	Fe-C	1.99	S3
	C-Fe-C	180.0	S3
$Fe(CO)_2(NO)_2$	Fe-C	1.82	S4
	Fe-N	1.68	S4
	C-Fe-C	98.7	S4
	N-Fe-N	109.0	S4
$FeC_6N_6H_{24}^{2+}$ ($Fe(II)en)_3$)	Fe-N	2.13	S4
$FeC_7NH_5O_5$ (CNOFEA)	Fe-C	1.79	S14
	Fe-C	2.09	S14
	Fe-O	1.97	S14
$FeC_8NH_5O_2$ (ACODUR)	Fe-C	1.91	S14
	Fe-C	1.78	S14
	Fe-C	2.19	S14
	C-Fe-C	89.2	S14
$FeC_9NH_8O_2^+$ (CPACFE)	Fe-N	1.91	S14
	Fe-C	1.77	S14
$FeC_{10}N_4H_{10}O_6$ (Diaqua-bis(pyrazinecarboxylato)-iron)	Fe-O	2.11	S17
	Fe-N	2.12	S17
	Fe-OH_2	2.14	S17
	O-Fe-N	78.1	S17
$FeC_{10}N_2H_{12}O_8^-$ (Iron(III)EDTA)	Fe-N	2.03	S4
$FeC_{16}N_5H_{11}O_4$ (FeN3O2)	Fe-O	2.12	S4
	Fe-O	1.92	S4
	Fe-N	1.89	S4
	O-Fe-O	81.4	S4
$FeC_{17}N_2H_{16}$ (Toluene-(2,2'-bipyridine)-iron)	Fe-N	1.90	S18
	Fe-C	2.11	S18
	N-Fe-N	81.9	S18
	N-Fe-C	122.8	S18

$FeC_{20}H_{12}N_4$ (iron porphyrin)	Fe-N	1.97	S4
$FeC_{36}N_6H_{24}^{+}$ (ferrous tris(ortophenantholine)	Fe-N	2.05	S4
FeF	Fe-F	1.76	S4
$Fe(II)(H_2O)_5F^{+}$	Fe-F	1.89	S4
	Fe-O	2.05	S4
FeF_2	Fe-F	1.77	S4
FeO_2F_2 (iron(VI)difluoride dioxide)	Fe-F	1.74	S4
	Fe=O	1.58	S4
FeF_3	Fe-F	1.78	S3
FeF_6^{3-}	Fe-F	2.06	S4
FeAl	Fe-Al	2.30	S3
$Fe(AlH_2)_2$	Fe-Al	2.47	S3
FeSiH	Fe-Si	2.30	S3
$FeSiH_2$	Fe-Si	2.26	S3
$Fe(SiH_3)_2$	Fe-Si	2.52	S3
FeP	Fe-P	2.23	S3
FePH	Fe-P	2.20	S3
$FeC_{12}P_4H_{34}S_2$ (JIYFAY)	Fe-S	2.35	S14
	Fe-P	2.23	S14
	P-Fe-S	89.4	S14
FeS	Fe-S	2.04	S3
$Fe(SH)_2$	Fe-S	2.25	S3
$FeC_9H_{10}SO_2$ (CEYTFE)	Fe-S	2.30	S4
	Fe-C(O)	1.75	S4
	Fe-C(C_4)	2.12	S4
	C-Fe-S	90.7	S4
$FeC_{16}N_2H_{18}S_2O_2$ (dicarbonyl ethylenediamine bis(phenylthiolato)iron)	Fe-S	2.33	S19
	Fe-S	2.34	S19
	Fe-N	2.04	S19
	Fe-N	2.03	S19
	Fe-C	1.76	S19
	N-Fe-S	86.8	S19
	C-Fe-S	93.2	S19
$FeC_9N_3H_{18}S_3O_3$ (tris(N,N-dimethylthiocarbamato)iron(III))	Fe-S	2.43	S20
	Fe-O	2.09	S20
	S-Fe-O	68.9	S20
	S-Fe-S	103.1	S20
Fe_4S_4	Fe-S	2.27	S3
$FeC_{12}H_{14}S_4O_2$ (CIBGAV10)	Fe-S	2.31	S14
	Fe-C	1.80	S14
	S-Fe-S	85.2	S14
	C-Fe-S	90.1	S14
$FeC_{14}N_6H_{16}S_6$ (diisothiocyanato-bisthiazoline iron(II))	Fe-N	2.19	S21
	Fe-N(CS)	2.08	S21
	N-Fe-N	73.9	S21
	SCN-Fe-NCS	97.4	S21
FeCl	Fe-Cl	2.13	S4

$Fe(II)(H_2O)_5Cl^+$	Fe-Cl	2.29	S4
	Fe-O	2.06	S4
$FeCl_2$	Fe-Cl	2.16	S4
$FeCl_3$	Fe-Cl	2.16	S3
$FeC_6N_2H_{18}Cl_3$ (FINJIV)	Fe-Cl	2.23	S14
	Fe-N	2.27	S14
	Cl-Fe-Cl	121.0	S14
$FeCl_4^-$	Fe-Cl	2.19	S4
$FeCl_4^{2-}$ (GOXLUA)	Fe-Cl	2.34	S14
$FeCl_6^{3-}$	Fe-Cl	2.53	S4
FeTi	Fe-Ti	2.54	S3
FeV	Fe-V	2.31	S3
FeCr	Fe-Cr	2.27	S3
FeMn	Fe-Mn	2.40	S3
FeCo	Fe-Co	2.31	S3
FeNi	Fe-Ni	2.33	S3
FeCu	Fe-Cu	2.31	S3
FeZn	Fe-Zn	2.53	S3
FeBr	Fe-Br	2.23	S4
$FeBr_2$	Fe-Br	2.31	S3
$FeC_6H_5BrO_3$ (ALCFEA)	Fe-Br	2.50	S14
	Fe-C(C_2)	2.13	S14
	Fe-C(O)	1.79	S14
	C-Fe-Br	88.6	S14
$Fe(H_2O)_5Br^+$	Fe-Br	2.42	S4
	Fe-O	2.06	S4
$Fe(H_2O)_4Br_2$	Fe-O	2.07	S4
	Fe-Br	2.50	S4
$FeC_4H_8BrO_7$ (Diaquabromo(oxydiacetato-O,O',O")-iron(III))	Fe-Br	2.37	S4
	Fe-O	2.00	S4
	Br-Fe-O	105.6	S4
$FeBr_2O_2$	Fe-Br	2.27	S4
	Fe=O	1.58	S4
	Br-Br-Fe	110.6	S4
FeZr	Fe-Zr	2.59	S3
FeMo	Fe-Mo	2.21	S3
FeI	Fe-I	2.44	S4
$Fe(CO)_3(C_3H_5)I$	Fe-I	2.75	S4
	Fe-C(O)	1.80	S4
	C-Fe-I	81.6	S4
$Fe(CO)_3(C_3H_5)I$ (ALCOFE10)	Fe-I	2.75	S14
	Fe-C	1.80	S14
	C-Fe-I	81.6	S14
FeI_2	Fe-I	2.50	S3

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