DFT calculations have been performed for $[Fe(SMe)_4]^{2-}$ and $[Fe(SeMe)_4]^{2-}$ in C_1 symmetry. Tables 1a, 1b, 2a and 2b give the charge decompositions for the major spins and minor spins of these systems, Figure 1 gives the MO diagrams of both complexes. Due to spin polarization, the major spin and minor spin levels greatly split in energy.

The highest energy major spin levels of $[Fe(SMe)_4]^{2-}$ are therefore of primarily S character and Fe-S antibonding (Table 1a and Figure 1). The lowest energy levels are primarily of Fe-d character and Fe-S bonding. In between is a block of Fe-S orbitals of mixed bonding-antibonding character.

The minor spin level scheme of $[Fe(SMe)_4]^{2-}$ exhibits the customary sequence of metal-ligand bonding and antibonding orbitals (Figure 1). The top of the scheme is made up of Fe-S antibonding orbitals (mainly Fe d character, Table 1b). At lower energy follows a block of Fe-S bonding orbitals (mainly S character).

The major and minor spin level schemes of $[Fe(SeMe)_4]^{2-}$ (Tables 2a and 2b, respectively) are quite similar. The salient difference between $[Fe(SMe)_4]^{2-}$ and $[Fe(SMe)_4]^{2-}$ is the fact that the highest occupied minor spin level has primarily Fe d character in case of $[Fe(SMe)_4]^{2-}$ and primarily ligand (Se) character in case of $[Fe(SeMe)_4]^{2-}$. This reflects the higher energy of the Se 4p as compared to the S 3p orbitals. Otherwise, charge decompositions are comparable for both systems, reflecting a similar degree of covalency for the Fe-S and the Fe-Se bond.

Table 1a. Major spin charge contribution of $[Fe(II)(SMe)_4]^{2-}$ with S=2.

character	label	energy [Hartree]	major spin charge decomposition [%]	
			Fe	S[a]
Fe-S antibonding	41	0.07899	12	77
	40	0.07681	7	80
	39	0.07515	10	77
	38	0.07036	4	84
	37	0.06036	6	78
	36	0.05877	5	78
	35	0.04999	5	75
	34	0.00712	1	69
nonbonding	33	-0.01137	85	6
antibonding	32	-0.03848	44	29
	31	-0.04725	34	32
Fe-S bonding	30	-0.05287	43	29
	29	-0.06865	6	35
	28	-0.07313	55	18
	27	-0.08112	94	3
	26	-0.08556	78	9
	25	-0.08946	80	8

[a] The charge decomposition gives the sum of all contributions of the S atoms.

Table 1b. Minor spin charge contribution of $[Fe(II)(SMe)_4]^{2-}$ with S=2.

character	label	energy [Hartree]	minor spin charge decomposition [%]	
			Fe	S[a]
Fe-S antibonding unoccupied	44	0.26965	62	10
	40	0.23501	32	13
	39	0.22815	40	15
	38	0.22050	75	10
Fe d_{z^2} Fe-S π bonding	37	0.07998	59	32
Fe-S π bonding	36	0.07210	3	84
	35	0.07102	7	79
	34	0.06390	7	81
Fe-S σ bonding	33	0.05759	24	65
	32	0.04483	12	72
	31	0.04362	9	76
	30	0.04218	26	62
S(p)	29	0.01429	0	72
S-Me σ bonding	28	-0.05557	1	43
	27	-0.05746	1	43
	26	-0.05907	3	43
	25	-0.06607	0	39

[a] The charge decomposition gives the sum of all contributions of the S atoms.

Table 2a. Major spin charge contribution of $[Fe(II)(SeMe)_4]^{2-}$ with S=2.

character	label	energy [Hartree]	major spin charge decomposition [%]	
			Fe	Se[a]
Fe-Se antibonding	41	0.07488	8	80
	40	0.07384	6	83
	39	0.07172	8	79
	38	0.06658	4	87
	37	0.05478	5	80
	36	0.05426	4	79
	35	0.04615	5	76
	34	-0.00152	1	68
non bonding	33	-0.02368	81	8
antibonding	32	-0.04430	24	36
	31	-0.05113	20	35
Fe-Se bonding	30	-0.05708	36	30
	29	-0.06664	3	33
	28	-0.07682	78	8
	27	-0.09222	91	4
	26	-0.09406	93	3
	25	-0.09711	92	3

[a] The charge decomposition gives the sum of all contributions of the Se atoms.

Table 2b. Minor spin charge contribution of $[Fe(II)(SeMe)_4]^{2-}$ with S=2.

character	label	energy [Hartree]	minor spin charge decomposition [%]	
			Fe	Se[a]
Fe-Se	44	0.25258	59	9
antibonding	40	0.21732	57	16
unoccuopied	39	0.21184	57	16
Fe d_{z^2}	38	0.20479	80	11
	37	0.07064	20	70
Fe-Se	36	0.06900	5	83
π bonding	35	0.06744	30	59
	34	0.06047	7	82
	33	0.05310	33	58
Fe-Se	32	0.04114	13	73
σ-bonding	31	0.04004	9	76
	30	0.03609	44	46
Se(p)	29	0.00590	0	71
	28	-0.05339	1	42
Se-Me	27	-0.05604	1	41
σ bonding	26	-0.05760	3	42
	25	-0.06398	0	35

[a] The charge decomposition gives the sum of all contributions of the Se atoms.

Density Functional Theory Calculations. Spin-unrestricted DFT calculations using Becke's three-parameter hybrid functional with the correlation functional of Lee, Yang and Parr (B3LYP)[1-3] were performed for the quintet ground state (S=2) of $Fe(SMe)_4^{2-}$ and $Fe(SeMe)_4^{2-}$. The models were optimized in C_1 symmetry, the resulting FeS_4 and $FeSe_4$ units have nearly T_d symmetry. The LanL2DZ basis set was used for the calculation, which applies Dunning/Huzinaga full double-ζ (D95) basis functions[4] on the first row and Los Alamos effective core potentials plus DZ functions on all other atoms.[5,6] Convergence was reached when the relative change in the density matrix between subsequent iterations was less than 1×10^{-8} for single points and optimizations. All computational procedures were used as they are implemented in the Gaussian 98 package.[7]

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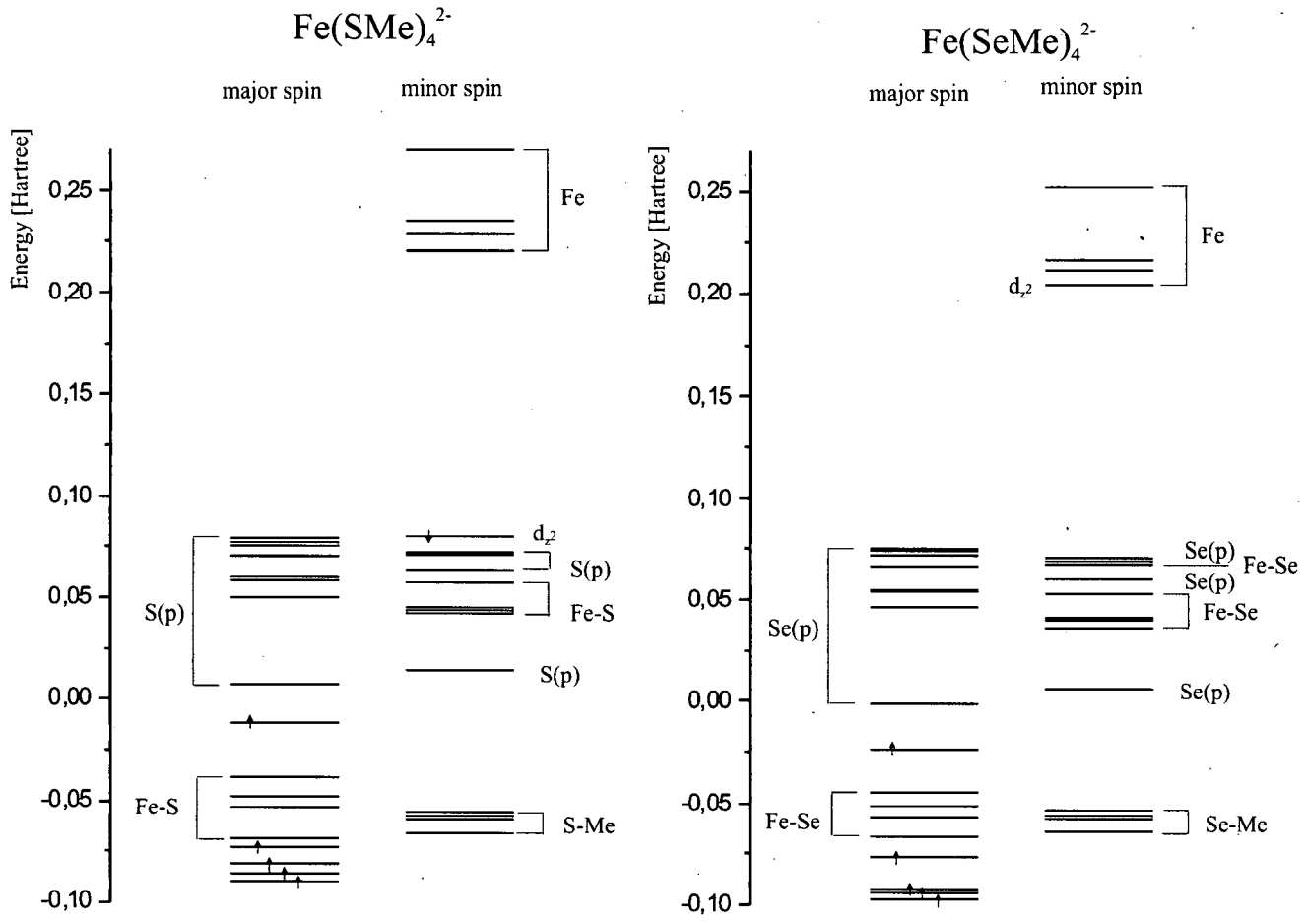

Figure 1. MO diagrams of $Fe(II)(SMe)_4^{2-}$ and $Fe(II)(SeMe)_4^{2-}$. Both model complexes were optimized in C_1 symmetry with S=2.

↑↓ denotes occupied d-orbitals