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## Protonation of bridging sulfur in cubanoid Fe<sub>4</sub>S<sub>4</sub> clusters causes large geometric changes: the theory of geometric and electronic structure.

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### Supplementary Information

#### Validation of the methodology

The ability of the DMol methodology used here to reproduce experimental data has been reported for the geometries of metal sulfide clusters<sup>1-3</sup> and for metal complexes of H, H<sub>2</sub> and N<sub>2</sub>.<sup>3</sup> Experimental reaction energy data relevant to metal sulfide clusters are sparse, but enthalpies of formation are reproduced well by DMol.<sup>3,4</sup> Delley *et al* report successful application of DMol to a collection of ground, excited and metastable states of transition metal nitrosyl complexes,<sup>5-8</sup> and of Ru-N<sub>2</sub> and Os-N<sub>2</sub> complexes.<sup>9</sup> Experimental metal carbonyl vibrational frequencies for models of the related [FeFe] hydrogenase enzymes are accurately calculated by DMol.<sup>10</sup> Spin densities in bridged Cu-Mn compounds, as measured by polarised neutron diffraction and as calculated by DMol, have been compared.<sup>11,12</sup>

For the [Fe<sub>4</sub>S<sub>4</sub>X<sub>4</sub>]<sup>2-</sup> clusters explored in this paper, the best comparisons are made with previous calculations using the broken symmetry method, and these comparisons are provided in Table S1 for [Fe<sub>4</sub>S<sub>4</sub>(SMe)<sub>4</sub>]<sup>2-</sup>.

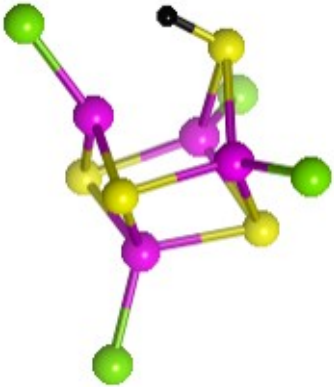
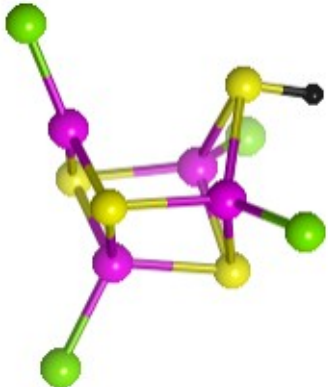
Table S1. Comparison of the atomic spin densities (Mulliken) and atomic charges (Mulliken) for the S=0 lowest energy state of [Fe<sub>4</sub>S<sub>4</sub>(SMe)<sub>4</sub>]<sup>2-</sup>, as calculated by the DMol procedure used here and by the broken symmetry method.<sup>13</sup> The Me groups bear negligible charge and spin).

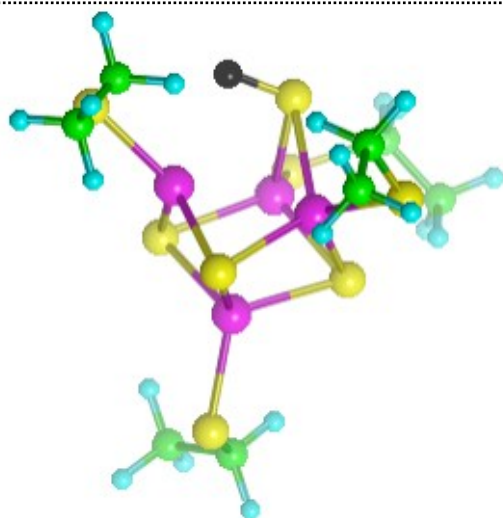
| atom              | DMol (no imposed symmetry)<br>fe4s4sme4.car_5 |                         | broken symmetry (C <sub>2v</sub> symmetry) <sup>13</sup> |                         |
|-------------------|---|-------------------------|--|-------------------------|
|                   | charge (Mulliken)                             | spin density (Mulliken) | charge (Mulliken)  | spin density (Mulliken) |
| Fe                | 0.645   | 3.103                   | +0.504 (x2)  | -3.127 (x2)             |
|                   | 0.642   | -3.092                  | +0.503 (x2)  | +3.127 (x2)             |
|                   | 0.638   | 3.064                   |  |                         |
|                   | 0.639   | -3.076                  |  |                         |
| μ <sub>3</sub> -S | -0.630  | -0.048                  | -0.550 (x2)  | -0.010 (x2)             |
|                   | -0.631  | 0.049                   | -0.550 (x2)  | +0.011 (x2)             |
|                   | -0.624  | 0.008                   |  |                         |
|                   | -0.629  | -0.010                  |  |                         |
| S (Me)            | -0.602  | 0.170                   | -0.546 (x2)  | -0.152 (x2)             |

|        |        |             |             |
|--------|--------|-------------|-------------|
| -0.599 | -0.167 | -0.545 (x2) | +0.152 (x2) |
| -0.600 | 0.174  |             |             |
| -0.599 | -0.177 |             |             |

### Coordinates of protonated clusters

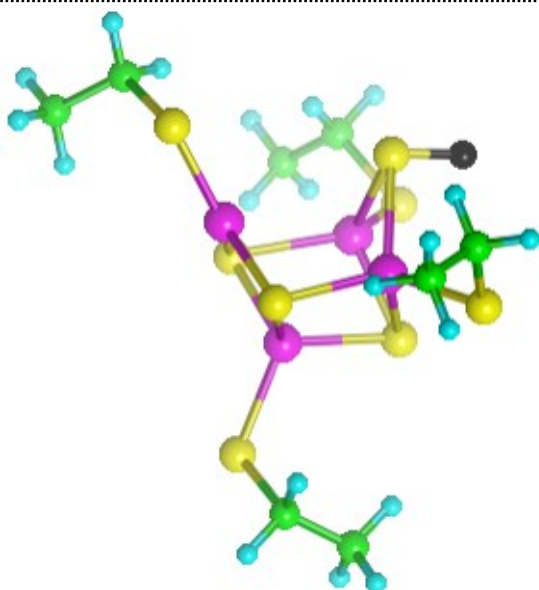
**Table S2.** Coordinates for ground state structures in Table 2 (for blyp functional only). The added proton is coloured black.

|  |    |    |        |        |        |
|--|----|----|--------|--------|--------|
|  <p><i>endo</i> [Fe<sub>4</sub>S<sub>3</sub>(SH)Cl<sub>4</sub>]<sup>-</sup> {opp / S=0}<br/>fe4s3shcl4cxa.car_4</p> | Cl | 1  | 1.375  | 1.438  | -3.385 |
|  | Cl | 2  | -2.693 | 2.784  | 0.802  |
|  | Cl | 3  | 2.736  | -0.102 | 3.007  |
|  | Cl | 4  | -1.016 | -3.665 | -0.145 |
|  | Fe | 5  | 0.659  | 0.631  | -1.441 |
|  | Fe | 6  | -1.376 | 1.021  | 0.438  |
|  | Fe | 7  | 1.280  | 0.167  | 1.361  |
|  | Fe | 8  | -0.483 | -1.513 | -0.103 |
|  | H  | 9  | 0.025  | 2.924  | 0.769  |
|  | S  | 10 | -1.541 | -0.124 | -1.550 |
|  | S  | 11 | 1.162  | 2.327  | 0.296  |
|  | S  | 12 | 1.787  | -1.081 | -0.535 |
|  | S  | 13 | -0.855 | -0.468 | 1.986  |
|  <p><i>exo</i> [Fe<sub>4</sub>S<sub>3</sub>(SH)Cl<sub>4</sub>]<sup>-</sup> {opp / S=0}<br/>fe4s4cl4pHd.car_3</p>  | Cl | 1  | -2.491 | 3.172  | 0.754  |
|  | Cl | 2  | 2.774  | -0.742 | 2.659  |
|  | Cl | 3  | 1.654  | 1.045  | -3.574 |
|  | Cl | 4  | -1.838 | -3.327 | -0.363 |
|  | Fe | 5  | -1.671 | 1.177  | 0.304  |
|  | Fe | 6  | 1.316  | -0.146 | 1.097  |
|  | Fe | 7  | 0.761  | 0.488  | -1.615 |
|  | Fe | 8  | -0.843 | -1.343 | -0.314 |
|  | H  | 9  | 2.926  | 1.827  | -0.285 |
|  | S  | 10 | -0.925 | -0.289 | 1.784  |
|  | S  | 11 | 1.628  | 2.016  | 0.083  |
|  | S  | 12 | -1.584 | 0.244  | -1.765 |
|  | S  | 13 | 1.416  | -1.492 | -0.795 |



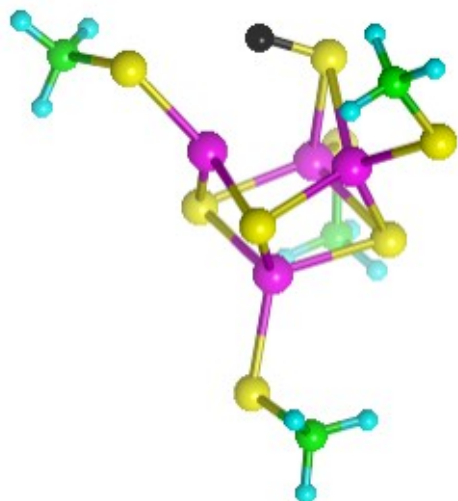
*endo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shset4ac.car\_4

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 41 |    |        |        |        |
| C  | 1  | 3.311  | 0.381  | -4.443 |
| C  | 2  | 2.289  | 1.504  | -4.231 |
| C  | 3  | -1.796 | -4.245 | -3.402 |
| C  | 4  | -0.600 | -4.407 | -2.457 |
| C  | 5  | -3.481 | 1.807  | 3.809  |
| C  | 6  | -2.757 | 2.637  | 2.743  |
| C  | 7  | 1.828  | 0.570  | 5.028  |
| C  | 8  | 1.983  | 1.401  | 3.748  |
| H  | 9  | -0.689 | 2.744  | -0.159 |
| Fe | 10 | 0.223  | 0.468  | -1.896 |
| Fe | 11 | -0.595 | -1.773 | -0.410 |
| Fe | 12 | -1.672 | 0.628  | 0.284  |
| Fe | 13 | 0.996  | 0.111  | 0.822  |
| H  | 14 | 3.091  | -0.182 | -5.360 |
| H  | 15 | -2.137 | -3.202 | -3.423 |
| H  | 16 | -2.640 | -4.871 | -3.080 |
| H  | 17 | -4.570 | 1.875  | 3.683  |
| H  | 18 | 2.789  | 0.130  | 5.327  |
| H  | 19 | 1.463  | 1.201  | 5.857  |
| H  | 20 | 2.521  | 2.085  | -3.331 |
| H  | 21 | 2.294  | 2.200  | -5.082 |
| H  | 22 | -1.517 | -4.538 | -4.429 |
| H  | 23 | -0.258 | -5.451 | -2.437 |
| H  | 24 | 0.242  | -3.784 | -2.777 |
| H  | 25 | -3.225 | 2.166  | 4.820  |
| H  | 26 | -3.033 | 3.698  | 2.823  |
| H  | 27 | -1.671 | 2.564  | 2.859  |
| H  | 28 | 1.115  | -0.250 | 4.877  |
| H  | 29 | 1.024  | 1.833  | 3.443  |
| H  | 30 | 2.687  | 2.229  | 3.905  |
| H  | 31 | -3.197 | 0.749  | 3.734  |
| H  | 32 | 4.329  | 0.797  | -4.528 |
| H  | 33 | 3.296  | -0.323 | -3.601 |
| S  | 34 | 0.519  | 0.889  | -4.107 |
| S  | 35 | -1.004 | -3.980 | -0.674 |
| S  | 36 | -3.217 | 2.126  | 0.993  |
| S  | 37 | 2.671  | 0.392  | 2.322  |
| S  | 38 | -0.862 | -0.987 | 1.692  |
| S  | 39 | 0.591  | 2.277  | -0.329 |
| S  | 40 | 1.595  | -1.137 | -0.927 |
| S  | 41 | -1.937 | -0.331 | -1.689 |



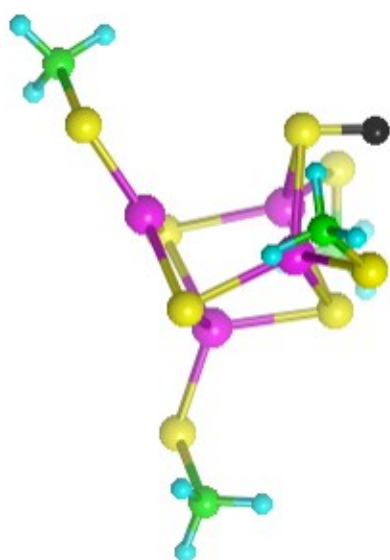
*exo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
 fe4s3shset4px11122a.car\_6

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 41 |    |        |        |        |
| C  | 1  | 2.393  | -0.361 | 5.015  |
| C  | 2  | 3.259  | 0.223  | 3.892  |
| C  | 3  | 0.939  | -5.424 | 0.114  |
| C  | 4  | -0.331 | -4.791 | 0.694  |
| C  | 5  | -0.362 | 1.798  | -5.226 |
| C  | 6  | 0.681  | 2.349  | -4.246 |
| C  | 7  | -4.685 | 2.762  | -0.256 |
| C  | 8  | -3.382 | 3.430  | 0.198  |
| H  | 9  | 3.004  | 1.938  | -0.143 |
| Fe | 10 | 1.623  | -0.282 | 1.089  |
| Fe | 11 | -0.385 | -1.593 | -0.283 |
| Fe | 12 | 0.961  | 0.438  | -1.552 |
| Fe | 13 | -1.514 | 0.683  | 0.648  |
| H  | 14 | 2.775  | -1.339 | 5.339  |
| H  | 15 | 1.673  | -4.653 | -0.153 |
| H  | 16 | 0.711  | -6.003 | -0.792 |
| H  | 17 | 0.123  | 1.288  | -6.070 |
| H  | 18 | -5.364 | 2.606  | 0.593  |
| H  | 19 | -5.200 | 3.390  | -1.004 |
| H  | 20 | 2.878  | 1.200  | 3.573  |
| H  | 21 | 4.293  | 0.367  | 4.236  |
| H  | 22 | 1.401  | -6.100 | 0.853  |
| H  | 23 | -1.057 | -5.567 | 0.971  |
| H  | 24 | -0.107 | -4.205 | 1.592  |
| H  | 25 | -0.984 | 2.615  | -5.628 |
| H  | 26 | 1.340  | 3.072  | -4.745 |
| H  | 27 | 0.200  | 2.860  | -3.405 |
| H  | 28 | -4.483 | 1.784  | -0.712 |
| H  | 29 | -2.696 | 3.566  | -0.646 |
| H  | 30 | -3.588 | 4.422  | 0.626  |
| H  | 31 | -1.021 | 1.076  | -4.728 |
| H  | 32 | 2.391  | 0.316  | 5.886  |
| H  | 33 | 1.357  | -0.495 | 4.682  |
| S  | 34 | 3.397  | -0.887 | 2.382  |
| S  | 35 | -1.227 | -3.677 | -0.519 |
| S  | 36 | 1.816  | 1.012  | -3.574 |
| S  | 37 | -2.476 | 2.501  | 1.558  |
| S  | 38 | -1.359 | 0.046  | -1.518 |
| S  | 39 | 1.690  | 1.959  | 0.217  |
| S  | 40 | -0.513 | -0.825 | 1.915  |
| S  | 41 | 1.832  | -1.499 | -0.874 |



*endo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(SMe)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shsme4n.car\_4

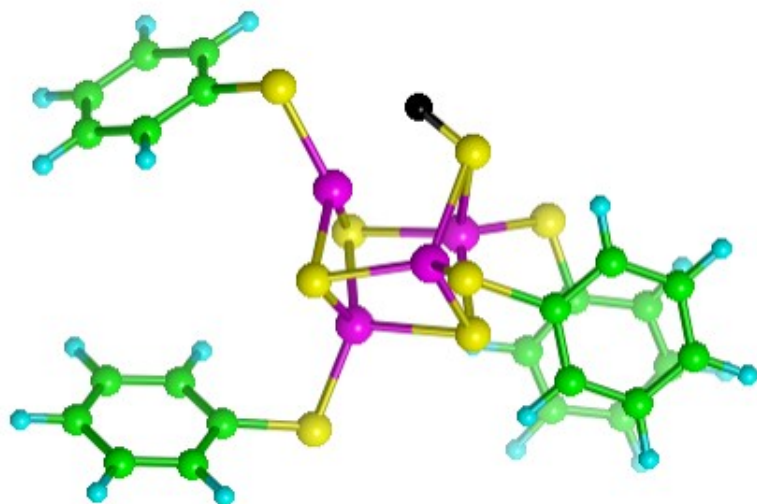
| 29 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | -4.162 | 2.668  | -0.066 |
| C  | 2  | 0.510  | -4.476 | 1.018  |
| C  | 3  | 2.075  | 2.149  | 3.844  |
| C  | 4  | 1.008  | -0.721 | -4.587 |
| H  | 5  | -0.454 | 3.006  | -0.023 |
| Fe | 6  | -1.445 | 0.875  | 0.560  |
| Fe | 7  | -0.205 | -1.457 | 0.002  |
| Fe | 8  | 1.289  | 0.571  | 1.071  |
| Fe | 9  | 0.545  | 0.688  | -1.639 |
| H  | 10 | -4.571 | 1.704  | -0.385 |
| H  | 11 | -4.970 | 3.298  | 0.324  |
| H  | 12 | -3.692 | 3.165  | -0.921 |
| H  | 13 | 0.415  | -5.564 | 0.909  |
| H  | 14 | 1.555  | -4.186 | 0.862  |
| H  | 15 | 0.195  | -4.180 | 2.025  |
| H  | 16 | 1.702  | 3.063  | 3.369  |
| H  | 17 | 1.244  | 1.618  | 4.322  |
| H  | 18 | 2.821  | 2.414  | 4.604  |
| H  | 19 | 1.743  | -1.373 | -4.103 |
| H  | 20 | 0.009  | -1.159 | -4.488 |
| H  | 21 | 1.255  | -0.612 | -5.651 |
| S  | 22 | -1.604 | -0.172 | -1.375 |
| S  | 23 | -0.486 | -0.547 | 2.067  |
| S  | 24 | 0.842  | 2.618  | -0.247 |
| S  | 25 | 1.968  | -0.786 | -0.560 |
| S  | 26 | -2.920 | 2.427  | 1.310  |
| S  | 27 | -0.587 | -3.681 | -0.267 |
| S  | 28 | 2.903  | 1.051  | 2.584  |
| S  | 29 | 1.048  | 0.977  | -3.819 |



*exo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(SMe)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shsme4.car\_4

| 29 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | -3.353 | 3.668  | 0.095  |
| C  | 2  | -0.611 | -4.589 | -0.164 |
| C  | 3  | 1.626  | 0.532  | 4.507  |
| C  | 4  | 1.891  | 0.216  | -4.389 |
| H  | 5  | 2.610  | 2.402  | 0.539  |
| Fe | 6  | -1.728 | 0.803  | 0.540  |
| Fe | 7  | -0.462 | -1.337 | -0.467 |
| Fe | 8  | 1.102  | 0.061  | 1.293  |
| Fe | 9  | 0.916  | 0.967  | -1.319 |
| H  | 10 | -3.803 | 3.120  | -0.738 |
| H  | 11 | -4.082 | 4.373  | 0.511  |
| H  | 12 | -2.473 | 4.216  | -0.257 |
| H  | 13 | -0.983 | -5.560 | -0.514 |
| H  | 14 | 0.480  | -4.631 | -0.077 |
| H  | 15 | -1.048 | -4.364 | 0.815  |
| H  | 16 | 1.493  | 1.606  | 4.341  |
| H  | 17 | 0.648  | 0.062  | 4.661  |
| H  | 18 | 2.251  | 0.375  | 5.395  |
| H  | 19 | 2.442  | -0.618 | -3.942 |
| H  | 20 | 0.863  | -0.096 | -4.604 |
| H  | 21 | 2.381  | 0.526  | -5.321 |

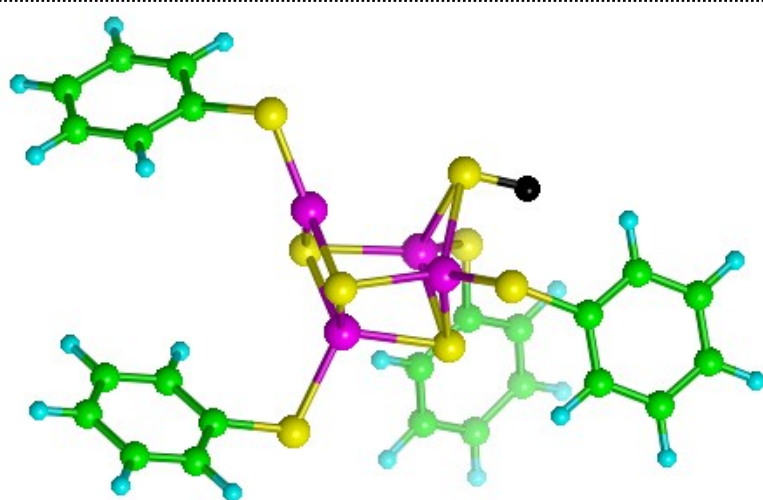
|   |    |        |        |        |
|---|----|--------|--------|--------|
| S | 22 | -1.378 | 0.482  | -1.609 |
| S | 23 | -0.977 | -0.957 | 1.728  |
| S | 24 | 1.248  | 2.386  | 0.577  |
| S | 25 | 1.832  | -1.007 | -0.527 |
| S | 26 | -2.868 | 2.497  | 1.473  |
| S | 27 | -1.121 | -3.299 | -1.412 |
| S | 28 | 2.497  | -0.249 | 3.052  |
| S | 29 | 1.892  | 1.678  | -3.229 |



*endo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(SPh)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shsph4o.car\_6

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 57 |    |        |        |        |
| C  | 1  | 3.702  | -0.167 | -2.909 |
| C  | 2  | 2.804  | -1.173 | -3.323 |
| C  | 3  | 3.274  | -2.303 | -4.006 |
| C  | 4  | 4.640  | -2.449 | -4.294 |
| C  | 5  | 5.538  | -1.454 | -3.880 |
| C  | 6  | 5.076  | -0.325 | -3.192 |
| C  | 7  | -3.466 | 3.861  | -0.070 |
| C  | 8  | -4.595 | 3.091  | 0.274  |
| C  | 9  | -5.710 | 3.045  | -0.572 |
| C  | 10 | -5.722 | 3.771  | -1.772 |
| C  | 11 | -4.606 | 4.549  | -2.114 |
| C  | 12 | -3.486 | 4.596  | -1.273 |
| C  | 13 | 3.323  | -0.356 | 4.166  |
| C  | 14 | 4.401  | 0.553  | 4.186  |
| C  | 15 | 5.723  | 0.088  | 4.157  |
| C  | 16 | 5.992  | -1.288 | 4.107  |
| C  | 17 | 4.923  | -2.197 | 4.088  |
| C  | 18 | 3.601  | -1.738 | 4.117  |
| C  | 19 | -3.122 | -2.576 | -0.362 |
| C  | 20 | -3.958 | -1.775 | -1.168 |
| C  | 21 | -5.341 | -1.746 | -0.948 |
| C  | 22 | -5.917 | -2.519 | 0.072  |
| C  | 23 | -5.091 | -3.324 | 0.872  |
| C  | 24 | -3.706 | -3.353 | 0.659  |
| H  | 25 | 0.684  | 3.533  | 0.979  |
| Fe | 26 | 1.491  | 1.084  | -0.615 |
| Fe | 27 | -0.991 | 1.954  | 0.633  |
| Fe | 28 | 0.926  | 0.515  | 2.119  |
| Fe | 29 | -0.545 | -0.670 | 0.129  |
| H  | 30 | 1.743  | -1.072 | -3.109 |
| H  | 31 | 2.566  | -3.072 | -4.314 |
| H  | 32 | 4.999  | -3.328 | -4.830 |
| H  | 33 | 6.604  | -1.557 | -4.086 |
| H  | 34 | 5.777  | 0.440  | -2.862 |
| H  | 35 | -4.585 | 2.521  | 1.201  |
| H  | 36 | -6.567 | 2.431  | -0.292 |
| H  | 37 | -6.587 | 3.728  | -2.433 |
| H  | 38 | -4.600 | 5.117  | -3.046 |
| H  | 39 | -2.616 | 5.190  | -1.548 |
| H  | 40 | 4.195  | 1.621  | 4.217  |
| H  | 41 | 6.545  | 0.805  | 4.163  |
| H  | 42 | 7.021  | -1.646 | 4.074  |
| H  | 43 | 5.117  | -3.269 | 4.043  |

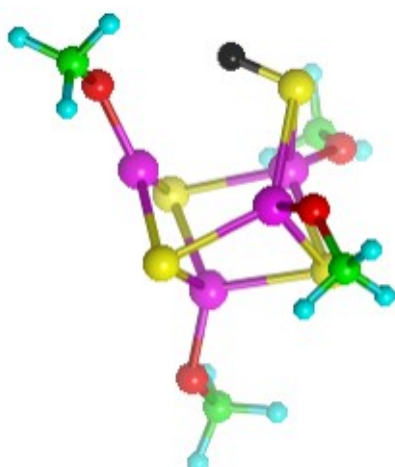
|   |    |        |        |        |
|---|----|--------|--------|--------|
| H | 44 | 2.771  | -2.443 | 4.093  |
| H | 45 | -3.515 | -1.167 | -1.954 |
| H | 46 | -5.968 | -1.110 | -1.573 |
| H | 47 | -6.992 | -2.489 | 0.247  |
| H | 48 | -5.524 | -3.927 | 1.671  |
| H | 49 | -3.065 | -3.967 | 1.290  |
| S | 50 | 1.729  | 2.663  | 1.168  |
| S | 51 | 3.188  | 1.346  | -2.086 |
| S | 52 | -0.684 | 1.128  | -1.390 |
| S | 53 | -2.046 | 3.945  | 1.050  |
| S | 54 | 1.745  | -0.866 | 0.575  |
| S | 55 | 1.614  | 0.229  | 4.277  |
| S | 56 | -1.364 | 0.193  | 2.049  |
| S | 57 | -1.340 | -2.669 | -0.656 |



*exo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(SPh)<sub>4</sub>]<sup>-</sup> {*opp* / S=0}  
fe4s3shsph4x.car\_5

|    |    |    |        |        |        |
|----|----|----|--------|--------|--------|
| 57 | C  | 1  | 2.276  | -0.393 | -3.963 |
|    | C  | 2  | 1.282  | -1.387 | -3.852 |
|    | C  | 3  | 1.357  | -2.555 | -4.621 |
|    | C  | 4  | 2.415  | -2.753 | -5.522 |
|    | C  | 5  | 3.400  | -1.761 | -5.647 |
|    | C  | 6  | 3.334  | -0.593 | -4.877 |
|    | C  | 7  | -3.456 | 3.987  | 1.086  |
|    | C  | 8  | -4.572 | 3.332  | 1.647  |
|    | C  | 9  | -5.848 | 3.494  | 1.092  |
|    | C  | 10 | -6.035 | 4.316  | -0.030 |
|    | C  | 11 | -4.930 | 4.973  | -0.591 |
|    | C  | 12 | -3.651 | 4.813  | -0.040 |
|    | C  | 13 | 4.756  | -0.336 | 2.818  |
|    | C  | 14 | 5.788  | 0.559  | 2.470  |
|    | C  | 15 | 7.028  | 0.079  | 2.027  |
|    | C  | 16 | 7.259  | -1.301 | 1.927  |
|    | C  | 17 | 6.234  | -2.197 | 2.268  |
|    | C  | 18 | 4.993  | -1.722 | 2.709  |
|    | C  | 19 | -3.006 | -2.549 | 0.837  |
|    | C  | 20 | -3.971 | -1.687 | 0.276  |
|    | C  | 21 | -5.257 | -1.607 | 0.827  |
|    | C  | 22 | -5.607 | -2.388 | 1.940  |
|    | C  | 23 | -4.654 | -3.255 | 2.496  |
|    | C  | 24 | -3.366 | -3.334 | 1.954  |
|    | H  | 25 | 3.498  | 2.293  | 0.240  |
|    | Fe | 26 | 1.260  | 0.965  | -0.992 |
|    | Fe | 27 | -1.039 | 1.836  | 1.124  |
|    | Fe | 28 | 1.760  | 0.520  | 1.724  |
|    | Fe | 29 | -0.361 | -0.687 | 0.502  |
|    | H  | 30 | 0.454  | -1.249 | -3.160 |
|    | H  | 31 | 0.584  | -3.315 | -4.511 |
|    | H  | 32 | 2.475  | -3.665 | -6.114 |
|    | H  | 33 | 4.232  | -1.897 | -6.341 |
|    | H  | 34 | 4.108  | 0.167  | -4.968 |
|    | H  | 35 | -4.430 | 2.691  | 2.516  |
|    | H  | 36 | -6.696 | 2.973  | 1.538  |
|    | H  | 37 | -7.027 | 4.438  | -0.463 |

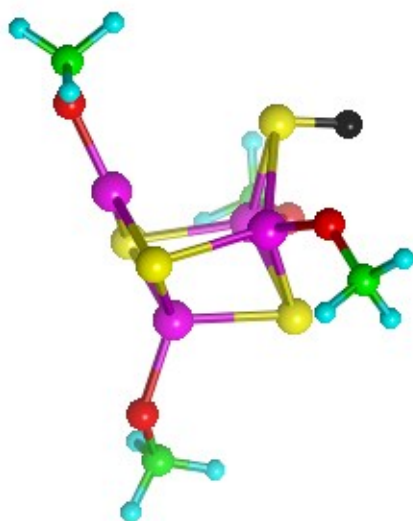
|   |    |        |        |        |
|---|----|--------|--------|--------|
| H | 38 | -5.060 | 5.613  | -1.465 |
| H | 39 | -2.795 | 5.317  | -0.483 |
| H | 40 | 5.609  | 1.631  | 2.550  |
| H | 41 | 7.813  | 0.785  | 1.754  |
| H | 42 | 8.222  | -1.675 | 1.577  |
| H | 43 | 6.398  | -3.272 | 2.185  |
| H | 44 | 4.196  | -2.416 | 2.966  |
| H | 45 | -3.705 | -1.078 | -0.586 |
| H | 46 | -5.986 | -0.928 | 0.384  |
| H | 47 | -6.608 | -2.319 | 2.367  |
| H | 48 | -4.910 | -3.867 | 3.362  |
| H | 49 | -2.623 | -3.997 | 2.393  |
| S | 50 | 2.194  | 2.588  | 0.498  |
| S | 51 | 2.252  | 1.139  | -3.026 |
| S | 52 | -1.093 | 1.029  | -0.927 |
| S | 53 | -1.824 | 3.839  | 1.855  |
| S | 54 | 1.888  | -0.979 | 0.070  |
| S | 55 | 3.192  | 0.272  | 3.485  |
| S | 56 | -0.394 | 0.235  | 2.585  |
| S | 57 | -1.353 | -2.724 | 0.130  |



*endo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(OMe)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shome4na.car\_3

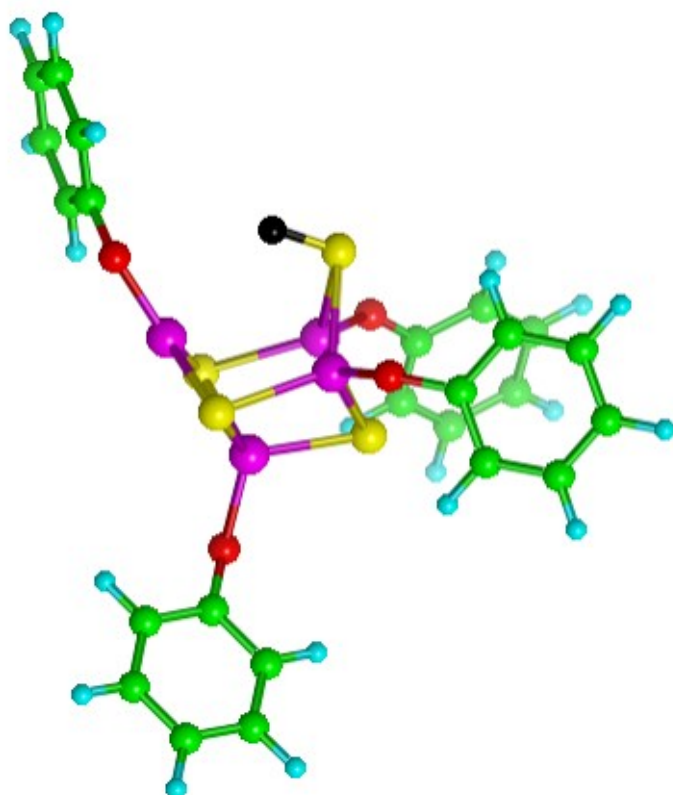
|    |    |        |        |        |
|----|----|--------|--------|--------|
| 29 |    |        |        |        |
| C  | 1  | 1.486  | 1.581  | -4.011 |
| C  | 2  | 1.958  | -0.994 | 3.942  |
| C  | 3  | -0.419 | -3.604 | -2.307 |
| C  | 4  | -3.180 | 2.885  | 2.150  |
| H  | 5  | -0.184 | 2.995  | 0.575  |
| Fe | 6  | 0.910  | 0.862  | -1.172 |
| Fe | 7  | 0.631  | 0.179  | 1.579  |
| Fe | 8  | -0.619 | -1.399 | -0.369 |
| Fe | 9  | -1.933 | 0.875  | 0.355  |
| H  | 10 | 1.345  | 2.671  | -4.151 |
| H  | 11 | 2.265  | 1.249  | -4.722 |
| H  | 12 | 0.538  | 1.083  | -4.285 |
| H  | 13 | 2.467  | -0.652 | 4.864  |
| H  | 14 | 1.193  | -1.739 | 4.235  |
| H  | 15 | 2.707  | -1.512 | 3.315  |
| H  | 16 | -0.684 | -2.994 | -3.193 |
| H  | 17 | 0.684  | -3.682 | -2.271 |
| H  | 18 | -0.825 | -4.622 | -2.465 |
| H  | 19 | -3.283 | 2.049  | 2.866  |
| H  | 20 | -2.488 | 3.624  | 2.597  |
| H  | 21 | -4.170 | 3.370  | 2.049  |
| O  | 22 | 1.888  | 1.290  | -2.688 |
| O  | 23 | 1.383  | 0.116  | 3.283  |
| O  | 24 | -0.952 | -3.064 | -1.115 |
| O  | 25 | -2.716 | 2.470  | 0.877  |
| S  | 26 | 1.053  | 2.444  | 0.694  |
| S  | 27 | 1.665  | -1.044 | -0.010 |
| S  | 28 | -1.321 | 0.407  | -1.745 |
| S  | 29 | -1.511 | -0.903 | 1.685  |





*exo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(OMe)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shome4.car\_5

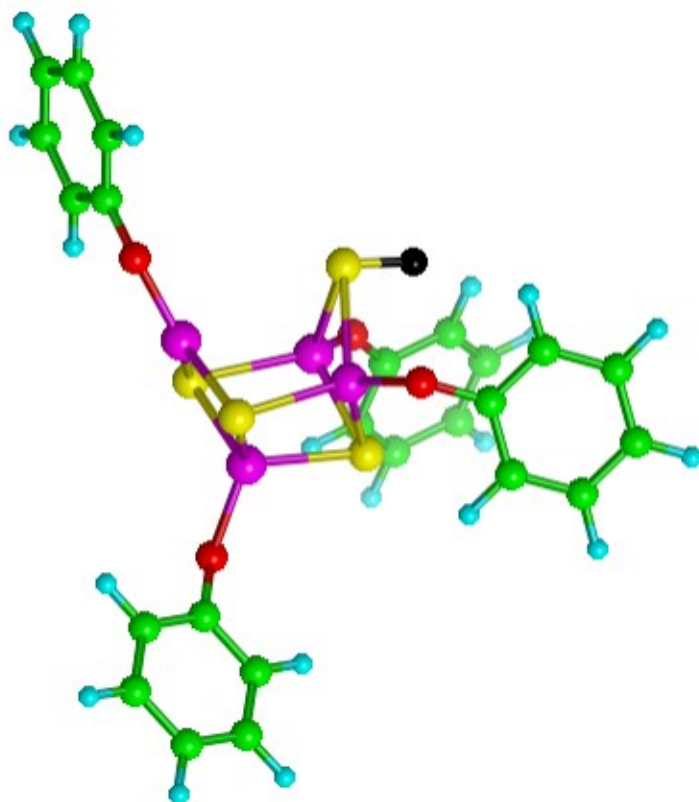
| 29 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 0.844  | 0.921  | -4.404 |
| C  | 2  | 2.865  | -0.604 | 3.487  |
| C  | 3  | -1.055 | -3.998 | -1.179 |
| C  | 4  | -2.731 | 3.540  | 1.886  |
| H  | 5  | 2.588  | 2.331  | -0.114 |
| Fe | 6  | 0.736  | 0.488  | -1.469 |
| Fe | 7  | 1.061  | 0.359  | 1.356  |
| Fe | 8  | -0.742 | -1.358 | 0.086  |
| Fe | 9  | -1.902 | 1.086  | 0.453  |
| H  | 10 | 0.766  | 2.020  | -4.516 |
| H  | 11 | 1.450  | 0.538  | -5.247 |
| H  | 12 | -0.175 | 0.504  | -4.499 |
| H  | 13 | 3.632  | -0.192 | 4.169  |
| H  | 14 | 2.152  | -1.190 | 4.098  |
| H  | 15 | 3.365  | -1.304 | 2.792  |
| H  | 16 | -1.453 | -3.628 | -2.144 |
| H  | 17 | 0.030  | -4.172 | -1.309 |
| H  | 18 | -1.533 | -4.975 | -0.969 |
| H  | 19 | -2.719 | 2.953  | 2.823  |
| H  | 20 | -1.870 | 4.235  | 1.915  |
| H  | 21 | -3.655 | 4.150  | 1.883  |
| O  | 22 | 1.456  | 0.568  | -3.179 |
| O  | 23 | 2.221  | 0.456  | 2.807  |
| O  | 24 | -1.326 | -3.107 | -0.117 |
| O  | 25 | -2.694 | 2.727  | 0.727  |
| S  | 26 | 1.230  | 2.381  | -0.002 |
| S  | 27 | 1.568  | -1.259 | -0.128 |
| S  | 28 | -1.595 | 0.131  | -1.542 |
| S  | 29 | -1.125 | -0.293 | 2.079  |



| 57 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 2.042  | 0.913  | -3.526 |
| C  | 2  | 1.735  | -0.218 | -4.322 |
| C  | 3  | 2.649  | -0.676 | -5.277 |
| C  | 4  | 3.882  | -0.029 | -5.463 |
| C  | 5  | 4.193  | 1.091  | -4.674 |
| C  | 6  | 3.289  | 1.561  | -3.718 |
| C  | 7  | -4.127 | 3.565  | 0.348  |
| C  | 8  | -4.484 | 3.521  | -1.021 |
| C  | 9  | -4.951 | 4.668  | -1.671 |
| C  | 10 | -5.081 | 5.884  | -0.983 |
| C  | 11 | -4.741 | 5.933  | 0.379  |
| C  | 12 | -4.275 | 4.793  | 1.042  |
| C  | 13 | 2.853  | -0.027 | 3.366  |
| C  | 14 | 3.785  | 1.032  | 3.486  |
| C  | 15 | 5.145  | 0.760  | 3.663  |
| C  | 16 | 5.609  | -0.564 | 3.725  |
| C  | 17 | 4.687  | -1.619 | 3.613  |
| C  | 18 | 3.324  | -1.361 | 3.435  |
| C  | 19 | -1.821 | -4.139 | 0.269  |
| C  | 20 | -3.073 | -4.379 | 0.890  |
| C  | 21 | -3.309 | -5.576 | 1.573  |

*endo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4s3shoph4.car\_8

|    |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 22 | -2.314 | -6.564 | 1.659  |
| C  | 23 | -1.071 | -6.333 | 1.046  |
| C  | 24 | -0.822 | -5.141 | 0.359  |
| H  | 25 | -0.700 | 3.008  | 0.911  |
| Fe | 26 | 0.203  | 0.969  | -1.089 |
| Fe | 27 | -2.672 | 0.960  | 0.569  |
| Fe | 28 | 0.428  | 0.332  | 1.703  |
| Fe | 29 | -1.152 | -1.241 | 0.057  |
| H  | 30 | 0.781  | -0.721 | -4.172 |
| H  | 31 | 2.398  | -1.550 | -5.880 |
| H  | 32 | 4.590  | -0.394 | -6.206 |
| H  | 33 | 5.149  | 1.601  | -4.802 |
| H  | 34 | 3.517  | 2.429  | -3.100 |
| H  | 35 | -4.370 | 2.582  | -1.562 |
| H  | 36 | -5.210 | 4.611  | -2.729 |
| H  | 37 | -5.438 | 6.776  | -1.498 |
| H  | 38 | -4.831 | 6.871  | 0.929  |
| H  | 39 | -4.006 | 4.825  | 2.097  |
| H  | 40 | 3.415  | 2.056  | 3.428  |
| H  | 41 | 5.850  | 1.589  | 3.746  |
| H  | 42 | 6.671  | -0.773 | 3.853  |
| H  | 43 | 5.035  | -2.652 | 3.659  |
| H  | 44 | 2.605  | -2.173 | 3.339  |
| H  | 45 | -3.841 | -3.609 | 0.825  |
| H  | 46 | -4.278 | -5.739 | 2.047  |
| H  | 47 | -2.502 | -7.493 | 2.195  |
| H  | 48 | -0.287 | -7.090 | 1.104  |
| H  | 49 | 0.140  | -4.956 | -0.120 |
| O  | 50 | 1.178  | 1.405  | -2.624 |
| O  | 51 | -3.661 | 2.487  | 1.014  |
| O  | 52 | 1.538  | 0.237  | 3.214  |
| O  | 53 | -1.599 | -3.010 | -0.432 |
| S  | 54 | 0.570  | 2.578  | 0.694  |
| S  | 55 | -2.038 | 0.319  | -1.455 |
| S  | 56 | 1.145  | -0.877 | -0.030 |
| S  | 57 | -1.753 | -0.452 | 2.119  |



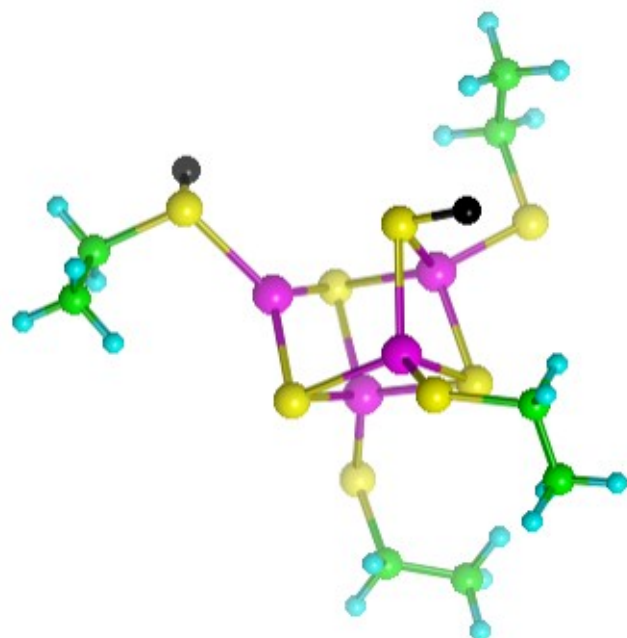
*exo* [Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>4</sub>]<sup>-</sup> {*opp* / S=0}  
 fe4s3shoph4x.car\_3

57

|    |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 1.425  | 0.707  | -3.887 |
| C  | 2  | 0.911  | -0.426 | -4.563 |
| C  | 3  | 1.578  | -0.945 | -5.678 |
| C  | 4  | 2.764  | -0.356 | -6.147 |
| C  | 5  | 3.280  | 0.766  | -5.478 |
| C  | 6  | 2.625  | 1.295  | -4.362 |
| C  | 7  | -3.843 | 3.809  | 1.026  |
| C  | 8  | -4.447 | 3.828  | -0.255 |
| C  | 9  | -5.004 | 5.010  | -0.757 |
| C  | 10 | -4.976 | 6.195  | -0.006 |
| C  | 11 | -4.385 | 6.181  | 1.269  |
| C  | 12 | -3.825 | 5.007  | 1.783  |
| C  | 13 | 3.393  | -0.019 | 2.785  |
| C  | 14 | 4.410  | 0.967  | 2.817  |
| C  | 15 | 5.759  | 0.593  | 2.799  |
| C  | 16 | 6.127  | -0.761 | 2.756  |
| C  | 17 | 5.122  | -1.742 | 2.733  |
| C  | 18 | 3.770  | -1.383 | 2.749  |
| C  | 19 | -2.004 | -4.054 | 0.718  |
| C  | 20 | -3.134 | -4.244 | 1.553  |
| C  | 21 | -3.304 | -5.440 | 2.258  |
| C  | 22 | -2.358 | -6.473 | 2.160  |
| C  | 23 | -1.232 | -6.290 | 1.339  |
| C  | 24 | -1.050 | -5.099 | 0.628  |
| H  | 25 | 1.942  | 2.611  | 0.133  |
| Fe | 26 | 0.044  | 0.886  | -1.165 |
| Fe | 27 | -2.447 | 1.150  | 0.970  |
| Fe | 28 | 0.716  | 0.365  | 1.547  |
| Fe | 29 | -1.224 | -1.187 | 0.303  |
| H  | 30 | -0.008 | -0.882 | -4.198 |
| H  | 31 | 1.168  | -1.819 | -6.184 |
| H  | 32 | 3.279  | -0.766 | -7.015 |
| H  | 33 | 4.204  | 1.232  | -5.825 |
| H  | 34 | 3.018  | 2.164  | -3.835 |
| H  | 35 | -4.461 | 2.911  | -0.842 |
| H  | 36 | -5.460 | 5.005  | -1.748 |
| H  | 37 | -5.402 | 7.115  | -0.406 |
| H  | 38 | -4.351 | 7.094  | 1.864  |
| H  | 39 | -3.355 | 4.987  | 2.766  |
| H  | 40 | 4.115  | 2.015  | 2.851  |
| H  | 41 | 6.527  | 1.368  | 2.813  |
| H  | 42 | 7.178  | -1.048 | 2.735  |
| H  | 43 | 5.393  | -2.799 | 2.696  |
| H  | 44 | 2.988  | -2.142 | 2.726  |
| H  | 45 | -3.865 | -3.439 | 1.626  |
| H  | 46 | -4.183 | -5.567 | 2.892  |
| H  | 47 | -2.493 | -7.402 | 2.713  |
| H  | 48 | -0.488 | -7.084 | 1.253  |
| H  | 49 | -0.180 | -4.951 | -0.011 |
| O  | 50 | 0.797  | 1.257  | -2.836 |
| O  | 51 | -3.300 | 2.696  | 1.559  |
| O  | 52 | 2.096  | 0.351  | 2.820  |

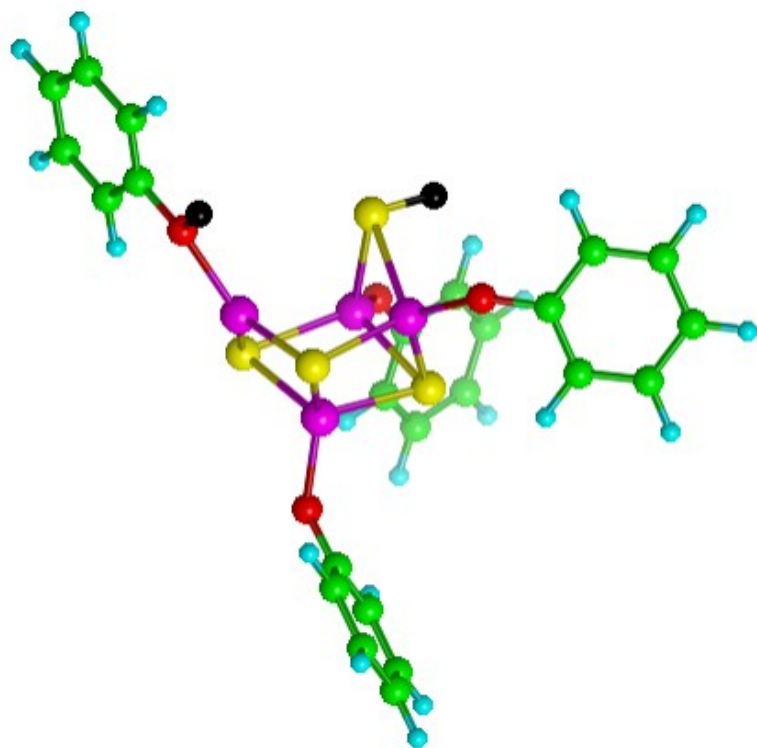
|   |    |        |        |        |
|---|----|--------|--------|--------|
| O | 53 | -1.864 | -2.933 | -0.012 |
| S | 54 | 0.623  | 2.566  | 0.475  |
| S | 55 | -2.264 | 0.389  | -1.103 |
| S | 56 | 1.040  | -0.982 | -0.204 |
| S | 57 | -1.386 | -0.287 | 2.400  |

**Table S3.** Coordinates for structures in Table 3 (for blyp functional only). The added protons are coloured black.



$[\text{Fe}_4\text{S}_3(\text{SH})(\text{SEt})_3(\text{HSEt})]^0$ , isomer **A<sup>ex</sup>** {opp / S=0}  
fe4s3shset4axa.car\_3

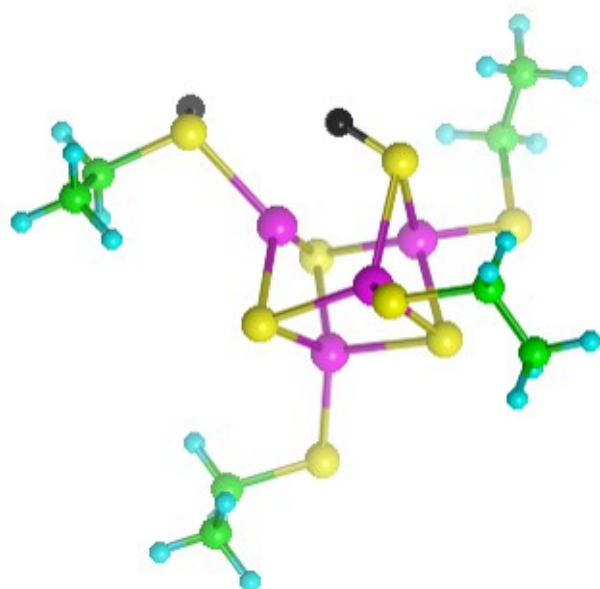
|    |    |        |        |        |
|----|----|--------|--------|--------|
| 42 |    |        |        |        |
| C  | 1  | 2.278  | 4.907  | -1.322 |
| C  | 2  | 2.181  | 3.839  | -2.415 |
| C  | 3  | 3.294  | -2.704 | 3.150  |
| C  | 4  | 2.819  | -1.304 | 3.547  |
| C  | 5  | 1.577  | -4.548 | -2.085 |
| C  | 6  | 0.079  | -4.284 | -1.905 |
| C  | 7  | -5.794 | 0.696  | 1.161  |
| C  | 8  | -5.449 | 1.593  | -0.027 |
| H  | 9  | 1.559  | 2.339  | 1.772  |
| H  | 10 | -3.734 | 3.090  | -0.933 |
| Fe | 11 | 1.009  | 1.212  | -0.826 |
| Fe | 12 | 0.350  | -0.368 | 1.434  |
| Fe | 13 | -0.376 | -1.119 | -1.113 |
| Fe | 14 | -2.093 | 0.749  | -0.323 |
| H  | 15 | 3.303  | 4.987  | -0.936 |
| H  | 16 | 3.067  | -2.914 | 2.097  |
| H  | 17 | 2.814  | -3.475 | 3.767  |
| H  | 18 | 1.852  | -4.567 | -3.148 |
| H  | 19 | -5.821 | 1.261  | 2.101  |
| H  | 20 | -6.787 | 0.255  | 0.999  |
| H  | 21 | 1.159  | 3.746  | -2.797 |
| H  | 22 | 2.829  | 4.089  | -3.265 |
| H  | 23 | 4.383  | -2.781 | 3.288  |
| H  | 24 | 3.064  | -1.088 | 4.595  |
| H  | 25 | 3.282  | -0.532 | 2.925  |
| H  | 26 | 1.841  | -5.522 | -1.645 |
| H  | 27 | -0.520 | -5.065 | -2.392 |
| H  | 28 | -0.203 | -4.261 | -0.847 |
| H  | 29 | -5.076 | -0.126 | 1.268  |
| H  | 30 | -5.419 | 1.036  | -0.968 |
| H  | 31 | -6.148 | 2.432  | -0.120 |
| H  | 32 | 2.179  | -3.774 | -1.594 |
| H  | 33 | 1.989  | 5.889  | -1.728 |
| H  | 34 | 1.615  | 4.675  | -0.478 |
| S  | 35 | 2.767  | 2.136  | -1.871 |
| S  | 36 | 0.953  | -1.103 | 3.456  |
| S  | 37 | -0.487 | -2.683 | -2.713 |
| S  | 38 | -3.746 | 2.378  | 0.224  |
| S  | 39 | -1.731 | -1.200 | 0.742  |
| S  | 40 | 1.736  | -0.887 | -0.227 |
| S  | 41 | 0.308  | 2.096  | 1.298  |
| S  | 42 | -0.903 | 0.902  | -2.146 |



[Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>3</sub>(HOPh)]<sup>0</sup>, isomer A<sup>ex</sup> {opp / S=0}  
 fe4s3shxoph4ha.car\_7

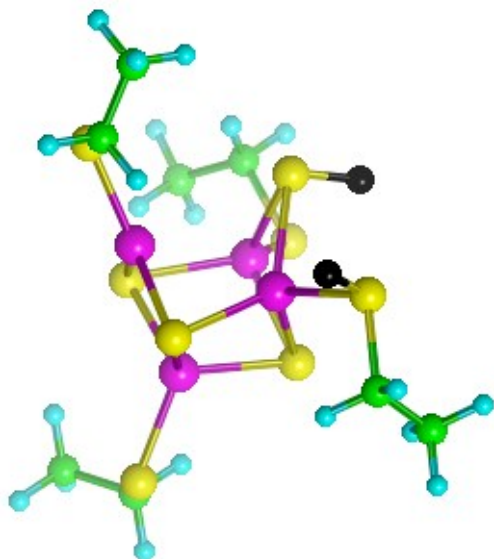
| 58 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 0.677  | 0.425  | -4.019 |
| C  | 2  | 0.273  | -0.871 | -4.417 |
| C  | 3  | 0.857  | -1.471 | -5.537 |
| C  | 4  | 1.843  | -0.800 | -6.279 |
| C  | 5  | 2.244  | 0.488  | -5.886 |
| C  | 6  | 1.672  | 1.099  | -4.767 |
| C  | 7  | -4.555 | 3.337  | 1.422  |
| C  | 8  | -5.186 | 3.016  | 0.222  |
| C  | 9  | -6.024 | 3.971  | -0.368 |
| C  | 10 | -6.224 | 5.219  | 0.240  |
| C  | 11 | -5.576 | 5.517  | 1.446  |
| C  | 12 | -4.732 | 4.572  | 2.048  |
| C  | 13 | 3.506  | 0.851  | 2.584  |
| C  | 14 | 4.356  | 1.980  | 2.638  |
| C  | 15 | 5.744  | 1.813  | 2.665  |
| C  | 16 | 6.308  | 0.527  | 2.644  |
| C  | 17 | 5.465  | -0.596 | 2.599  |
| C  | 18 | 4.075  | -0.444 | 2.570  |
| C  | 19 | -0.683 | -4.257 | 0.712  |
| C  | 20 | -0.731 | -4.644 | 2.072  |
| C  | 21 | -0.156 | -5.853 | 2.477  |
| C  | 22 | 0.478  | -6.691 | 1.545  |
| C  | 23 | 0.528  | -6.308 | 0.194  |
| C  | 24 | -0.047 | -5.105 | -0.225 |
| H  | 25 | -3.371 | 2.682  | 2.870  |
| H  | 26 | 1.248  | 3.046  | -0.192 |
| Fe | 27 | -0.324 | 0.797  | -1.184 |
| Fe | 28 | -2.605 | 0.723  | 1.233  |
| Fe | 29 | 0.727  | 0.679  | 1.471  |
| Fe | 30 | -1.013 | -1.290 | 0.521  |
| H  | 31 | -0.493 | -1.387 | -3.839 |
| H  | 32 | 0.540  | -2.470 | -5.835 |
| H  | 33 | 2.293  | -1.272 | -7.151 |
| H  | 34 | 3.009  | 1.018  | -6.454 |
| H  | 35 | 1.976  | 2.096  | -4.451 |
| H  | 36 | -5.020 | 2.047  | -0.247 |
| H  | 37 | -6.519 | 3.734  | -1.308 |
| H  | 38 | -6.877 | 5.955  | -0.225 |
| H  | 39 | -5.719 | 6.484  | 1.923  |
| H  | 40 | -4.220 | 4.804  | 2.982  |
| H  | 41 | 3.905  | 2.972  | 2.655  |
| H  | 42 | 6.389  | 2.690  | 2.701  |
| H  | 43 | 7.390  | 0.401  | 2.661  |
| H  | 44 | 5.894  | -1.598 | 2.587  |
| H  | 45 | 3.415  | -1.310 | 2.536  |
| H  | 46 | -1.228 | -3.991 | 2.788  |
| H  | 47 | -0.205 | -6.146 | 3.526  |
| H  | 48 | 0.925  | -7.631 | 1.866  |
| H  | 49 | 1.018  | -6.952 | -0.536 |
| H  | 50 | -0.014 | -4.796 | -1.269 |

|   |    |        |        |        |
|---|----|--------|--------|--------|
| O | 51 | 0.122  | 1.049  | -2.958 |
| O | 52 | -3.710 | 2.352  | 2.017  |
| O | 53 | 2.165  | 1.034  | 2.579  |
| O | 54 | -1.271 | -3.115 | 0.290  |
| S | 55 | 0.014  | 2.696  | 0.265  |
| S | 56 | -2.510 | -0.050 | -0.805 |
| S | 57 | 1.112  | -0.733 | -0.200 |
| S | 58 | -1.156 | -0.296 | 2.601  |



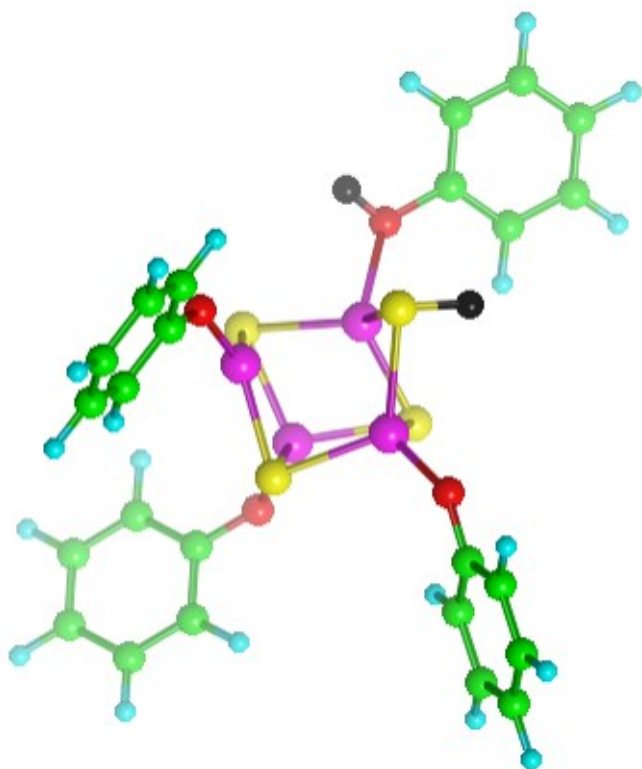
[Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>3</sub>(HSEt)]<sup>0</sup>, isomer A<sup>en</sup> {opp / S=0}  
fe4s3shset4an.car\_4

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 42 |    |        |        |        |
| C  | 1  | 3.549  | 3.735  | -2.511 |
| C  | 2  | 3.167  | 2.514  | -3.353 |
| C  | 3  | 3.764  | -1.530 | 3.706  |
| C  | 4  | 2.894  | -0.298 | 3.971  |
| C  | 5  | -2.259 | -4.926 | -0.384 |
| C  | 6  | -2.019 | -4.089 | -1.644 |
| C  | 7  | -4.875 | 1.383  | 1.135  |
| C  | 8  | -4.456 | 1.845  | -0.261 |
| H  | 9  | 0.104  | 2.805  | 0.619  |
| H  | 10 | -2.714 | 3.058  | -1.487 |
| Fe | 11 | 1.576  | 0.614  | -1.187 |
| Fe | 12 | 0.733  | -0.259 | 1.424  |
| Fe | 13 | -0.070 | -1.524 | -0.885 |
| Fe | 14 | -1.106 | 0.870  | -0.383 |
| H  | 15 | 4.580  | 3.654  | -2.144 |
| H  | 16 | 3.727  | -1.822 | 2.649  |
| H  | 17 | 3.434  | -2.385 | 4.310  |
| H  | 18 | -1.609 | -5.811 | -0.370 |
| H  | 19 | -4.915 | 2.222  | 1.842  |
| H  | 20 | -5.878 | 0.939  | 1.076  |
| H  | 21 | 2.134  | 2.575  | -3.715 |
| H  | 22 | 3.819  | 2.425  | -4.231 |
| H  | 23 | 4.813  | -1.309 | 3.964  |
| H  | 24 | 2.924  | -0.018 | 5.032  |
| H  | 25 | 3.229  | 0.566  | 3.387  |
| H  | 26 | -3.306 | -5.267 | -0.352 |
| H  | 27 | -2.223 | -4.673 | -2.550 |
| H  | 28 | -2.661 | -3.201 | -1.665 |
| H  | 29 | -4.190 | 0.621  | 1.529  |
| H  | 30 | -4.406 | 1.017  | -0.974 |
| H  | 31 | -5.121 | 2.624  | -0.648 |
| H  | 32 | -2.059 | -4.342 | 0.523  |
| H  | 33 | 3.472  | 4.650  | -3.119 |
| H  | 34 | 2.889  | 3.842  | -1.641 |
| S  | 35 | 3.386  | 0.874  | -2.462 |
| S  | 36 | 1.069  | -0.566 | 3.613  |
| S  | 37 | -0.230 | -3.542 | -1.827 |
| S  | 38 | -2.741 | 2.640  | -0.195 |
| S  | 39 | -1.411 | -0.983 | 0.870  |
| S  | 40 | 2.088  | -1.282 | -0.024 |
| S  | 41 | 1.249  | 2.067  | 0.715  |
| S  | 42 | -0.347 | 0.289  | -2.354 |



[Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>3</sub>(HSEt)]<sup>0</sup>, isomer **B<sup>ex</sup>** {opp / S=0}  
 fe4s3shhsetbx.car\_4

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 42 |    |        |        |        |
| C  | 1  | -1.591 | 4.185  | 3.800  |
| C  | 2  | -2.155 | 2.822  | 3.386  |
| C  | 3  | -0.698 | 2.035  | -4.974 |
| C  | 4  | 0.521  | 2.376  | -4.113 |
| C  | 5  | -2.861 | -3.435 | -3.012 |
| C  | 6  | -1.531 | -3.863 | -2.385 |
| C  | 7  | 4.027  | -2.672 | 2.557  |
| C  | 8  | 3.038  | -1.953 | 3.475  |
| H  | 9  | 2.717  | 2.004  | -0.062 |
| H  | 10 | 2.094  | 0.253  | 3.987  |
| Fe | 11 | -1.545 | 0.781  | 0.828  |
| Fe | 12 | 0.608  | 0.545  | -1.374 |
| Fe | 13 | -0.700 | -1.591 | -0.084 |
| Fe | 14 | 1.133  | -0.077 | 1.180  |
| H  | 15 | -2.239 | 5.003  | 3.459  |
| H  | 16 | -1.472 | 1.528  | -4.383 |
| H  | 17 | -0.421 | 1.377  | -5.809 |
| H  | 18 | -3.702 | -3.986 | -2.572 |
| H  | 19 | 5.018  | -2.202 | 2.587  |
| H  | 20 | 4.132  | -3.714 | 2.889  |
| H  | 21 | -1.503 | 2.002  | 3.704  |
| H  | 22 | -3.148 | 2.655  | 3.820  |
| H  | 23 | -1.132 | 2.957  | -5.392 |
| H  | 24 | 1.290  | 2.893  | -4.702 |
| H  | 25 | 0.251  | 3.026  | -3.273 |
| H  | 26 | -2.846 | -3.636 | -4.095 |
| H  | 27 | -1.353 | -4.936 | -2.532 |
| H  | 28 | -0.686 | -3.319 | -2.819 |
| H  | 29 | 3.674  | -2.684 | 1.518  |
| H  | 30 | 2.044  | -2.409 | 3.450  |
| H  | 31 | 3.399  | -1.914 | 4.508  |
| H  | 32 | -3.040 | -2.362 | -2.864 |
| H  | 33 | -1.518 | 4.244  | 4.898  |
| H  | 34 | -0.591 | 4.346  | 3.377  |
| S  | 35 | -2.390 | 2.716  | 1.520  |
| S  | 36 | 1.391  | 0.848  | -3.444 |
| S  | 37 | -1.485 | -3.626 | -0.522 |
| S  | 38 | 2.852  | -0.154 | 2.936  |
| S  | 39 | 1.535  | -1.409 | -0.565 |
| S  | 40 | -1.679 | 0.159  | -1.275 |
| S  | 41 | 1.399  | 2.135  | 0.267  |
| S  | 42 | -0.837 | -0.948 | 2.102  |

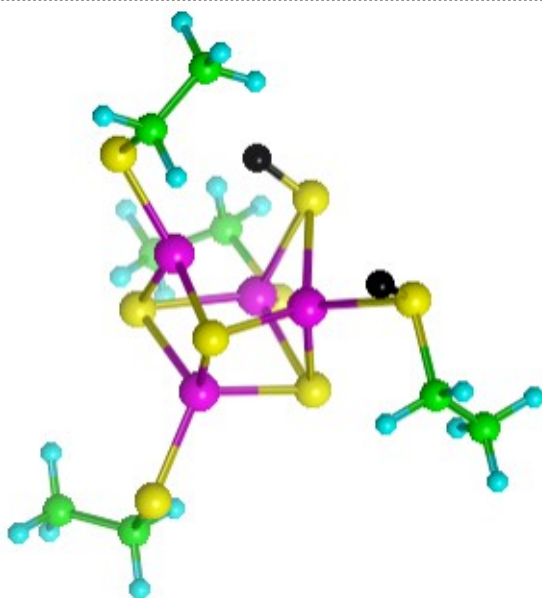


[Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>3</sub>(HOPh)]<sup>0</sup>, isomer **B<sup>ex</sup>** {opp / S=0}  
 fe4s3shnoph4ha.car\_6

| 58 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 2.719  | -2.722 | 1.710  |
| C  | 2  | 2.551  | -3.653 | 0.659  |
| C  | 3  | 2.977  | -4.975 | 0.823  |
| C  | 4  | 3.573  | -5.392 | 2.024  |
| C  | 5  | 3.740  | -4.467 | 3.069  |
| C  | 6  | 3.319  | -3.143 | 2.921  |
| C  | 7  | 2.392  | 4.326  | -2.282 |
| C  | 8  | 3.470  | 3.566  | -2.741 |
| C  | 9  | 4.687  | 4.211  | -2.994 |
| C  | 10 | 4.816  | 5.594  | -2.796 |
| C  | 11 | 3.720  | 6.335  | -2.335 |
| C  | 12 | 2.497  | 5.702  | -2.070 |
| C  | 13 | -2.880 | 1.664  | 2.940  |
| C  | 14 | -2.657 | 2.479  | 4.073  |
| C  | 15 | -3.277 | 2.173  | 5.288  |
| C  | 16 | -4.130 | 1.063  | 5.397  |
| C  | 17 | -4.358 | 0.257  | 4.271  |
| C  | 18 | -3.741 | 0.548  | 3.051  |
| C  | 19 | -2.363 | -2.451 | -2.964 |
| C  | 20 | -3.482 | -1.851 | -3.587 |
| C  | 21 | -4.661 | -2.582 | -3.759 |
| C  | 22 | -4.747 | -3.913 | -3.320 |
| C  | 23 | -3.635 | -4.511 | -2.704 |
| C  | 24 | -2.449 | -3.792 | -2.525 |
| H  | 25 | 0.431  | 4.278  | -1.981 |
| H  | 26 | 2.768  | 2.104  | 0.982  |
| Fe | 27 | 1.249  | -0.319 | 0.629  |
| Fe | 28 | 0.723  | 1.772  | -0.998 |
| Fe | 29 | -1.523 | 0.975  | 0.419  |
| Fe | 30 | -0.574 | -0.497 | -1.628 |
| H  | 31 | 2.094  | -3.325 | -0.273 |
| H  | 32 | 2.845  | -5.684 | 0.006  |
| H  | 33 | 3.902  | -6.423 | 2.145  |
| H  | 34 | 4.199  | -4.782 | 4.006  |
| H  | 35 | 3.438  | -2.417 | 3.723  |
| H  | 36 | 3.350  | 2.497  | -2.903 |
| H  | 37 | 5.532  | 3.628  | -3.357 |
| H  | 38 | 5.764  | 6.089  | -2.997 |
| H  | 39 | 3.812  | 7.408  | -2.174 |
| H  | 40 | 1.646  | 6.275  | -1.696 |
| H  | 41 | -1.991 | 3.337  | 3.978  |
| H  | 42 | -3.090 | 2.804  | 6.157  |
| H  | 43 | -4.614 | 0.832  | 6.345  |
| H  | 44 | -5.020 | -0.606 | 4.341  |
| H  | 45 | -3.918 | -0.076 | 2.176  |
| H  | 46 | -3.402 | -0.819 | -3.927 |
| H  | 47 | -5.518 | -2.111 | -4.241 |
| H  | 48 | -5.668 | -4.477 | -3.457 |
| H  | 49 | -3.693 | -5.544 | -2.362 |
| H  | 50 | -1.581 | -4.245 | -2.049 |
| O  | 51 | 2.342  | -1.430 | 1.599  |
| O  | 52 | 1.171  | 3.645  | -2.041 |

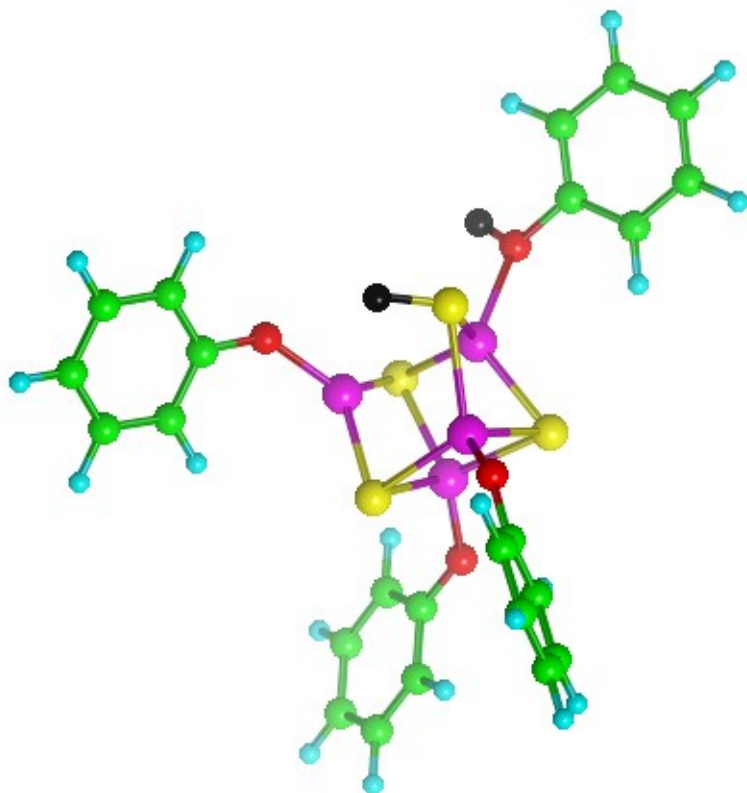


|   |    |        |        |        |
|---|----|--------|--------|--------|
| O | 53 | -2.285 | 1.986  | 1.764  |
| O | 54 | -1.207 | -1.760 | -2.819 |
| S | 55 | 1.436  | 2.036  | 1.269  |
| S | 56 | 1.724  | -0.114 | -1.636 |
| S | 57 | -0.935 | -1.133 | 0.612  |
| S | 58 | -1.488 | 1.629  | -1.760 |



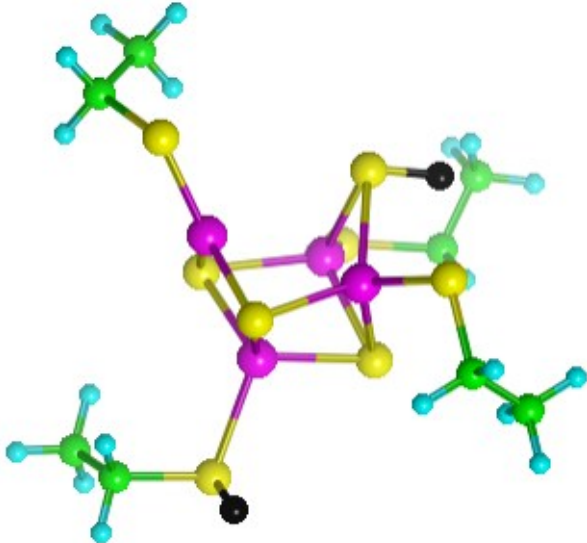
[Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>3</sub>(HSEt)]<sup>0</sup>, isomer **B<sup>en</sup>** {opp / S=0}  
fe4s3shhsetbn.car\_3

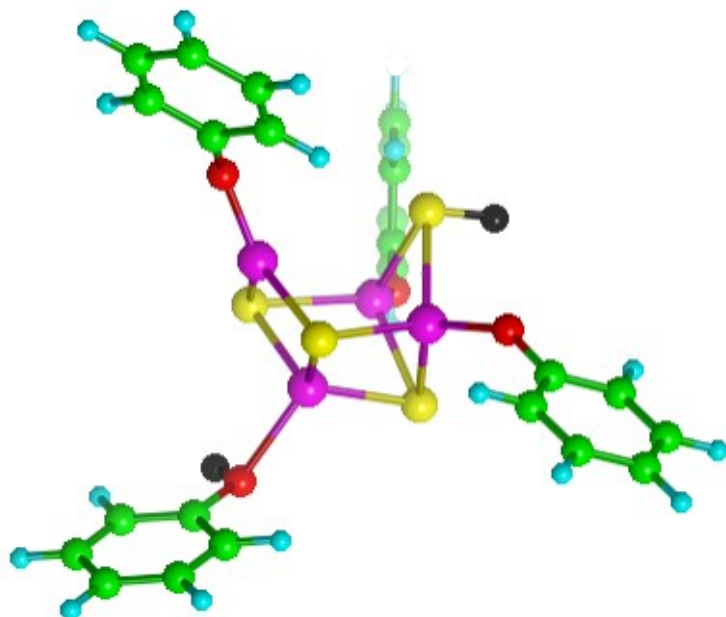
|    |    |        |        |        |
|----|----|--------|--------|--------|
| 42 |    |        |        |        |
| C  | 1  | -0.611 | 4.595  | 3.203  |
| C  | 2  | -1.604 | 3.428  | 3.239  |
| C  | 3  | -1.547 | 1.075  | -5.051 |
| C  | 4  | -0.227 | 1.577  | -4.460 |
| C  | 5  | -3.357 | -3.749 | -1.805 |
| C  | 6  | -1.948 | -4.130 | -1.340 |
| C  | 7  | 4.658  | -2.175 | 1.887  |
| C  | 8  | 3.758  | -1.572 | 2.966  |
| H  | 9  | 0.348  | 2.885  | 0.140  |
| H  | 10 | 2.706  | 0.521  | 3.682  |
| Fe | 11 | -1.177 | 1.101  | 0.861  |
| Fe | 12 | 0.364  | 0.304  | -1.485 |
| Fe | 13 | -0.719 | -1.520 | 0.350  |
| Fe | 14 | 1.336  | 0.085  | 1.065  |
| H  | 15 | -1.044 | 5.469  | 2.699  |
| H  | 16 | -2.191 | 0.649  | -4.272 |
| H  | 17 | -1.370 | 0.301  | -5.809 |
| H  | 18 | -4.121 | -4.171 | -1.139 |
| H  | 19 | 5.594  | -1.612 | 1.784  |
| H  | 20 | 4.908  | -3.208 | 2.166  |
| H  | 21 | -1.168 | 2.540  | 3.707  |
| H  | 22 | -2.505 | 3.700  | 3.803  |
| H  | 23 | -2.088 | 1.908  | -5.527 |
| H  | 24 | 0.426  | 1.991  | -5.239 |
| H  | 25 | -0.390 | 2.364  | -3.715 |
| H  | 26 | -3.533 | -4.136 | -2.820 |
| H  | 27 | -1.821 | -5.220 | -1.316 |
| H  | 28 | -1.179 | -3.715 | -2.000 |
| H  | 29 | 4.153  | -2.203 | 0.914  |
| H  | 30 | 2.821  | -2.125 | 3.079  |
| H  | 31 | 4.269  | -1.510 | 3.933  |
| H  | 32 | -3.485 | -2.660 | -1.824 |
| H  | 33 | -0.341 | 4.890  | 4.229  |
| H  | 34 | 0.311  | 4.320  | 2.674  |
| S  | 35 | -2.242 | 2.950  | 1.534  |
| S  | 36 | 0.787  | 0.202  | -3.676 |
| S  | 37 | -1.578 | -3.568 | 0.414  |
| S  | 38 | 3.318  | 0.208  | 2.512  |
| S  | 39 | 1.431  | -1.484 | -0.504 |
| S  | 40 | -1.860 | 0.063  | -0.955 |
| S  | 41 | 1.411  | 2.120  | -0.261 |
| S  | 42 | -0.495 | -0.490 | 2.360  |



[Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>3</sub>(HOPh)]<sup>0</sup>, isomer **B<sup>en</sup>** {opp / S=0}  
 fe4s3shoph4hbn.car\_3

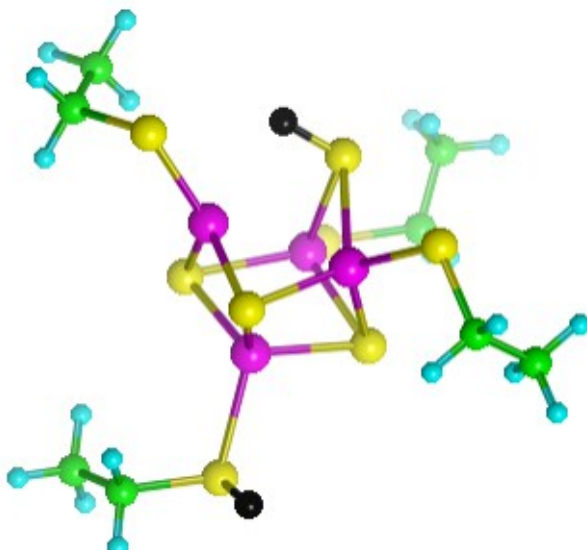
| 58 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 1.654  | -1.990 | 3.420  |
| C  | 2  | 2.160  | -3.051 | 2.633  |
| C  | 3  | 2.520  | -4.258 | 3.240  |
| C  | 4  | 2.383  | -4.432 | 4.627  |
| C  | 5  | 1.880  | -3.379 | 5.409  |
| C  | 6  | 1.514  | -2.168 | 4.817  |
| C  | 7  | 2.804  | 4.411  | -1.557 |
| C  | 8  | 3.983  | 3.877  | -1.034 |
| C  | 9  | 5.025  | 4.749  | -0.695 |
| C  | 10 | 4.887  | 6.132  | -0.884 |
| C  | 11 | 3.694  | 6.646  | -1.412 |
| C  | 12 | 2.639  | 5.785  | -1.749 |
| C  | 13 | -4.102 | 1.539  | 0.664  |
| C  | 14 | -4.745 | 2.602  | 1.341  |
| C  | 15 | -5.976 | 2.390  | 1.972  |
| C  | 16 | -6.590 | 1.128  | 1.936  |
| C  | 17 | -5.956 | 0.072  | 1.262  |
| C  | 18 | -4.723 | 0.268  | 0.632  |
| C  | 19 | 0.007  | -3.288 | -3.114 |
| C  | 20 | -0.670 | -2.972 | -4.315 |
| C  | 21 | -1.418 | -3.952 | -4.976 |
| C  | 22 | -1.505 | -5.254 | -4.456 |
| C  | 23 | -0.836 | -5.568 | -3.262 |
| C  | 24 | -0.084 | -4.599 | -2.591 |
| H  | 25 | 1.078  | 3.936  | -2.419 |
| H  | 26 | -0.822 | 2.545  | 1.459  |
| Fe | 27 | 0.843  | -0.022 | 1.294  |
| Fe | 28 | 1.040  | 1.717  | -0.832 |
| Fe | 29 | -1.475 | 0.747  | -0.502 |
| Fe | 30 | 0.501  | -0.838 | -1.478 |
| H  | 31 | 2.272  | -2.911 | 1.559  |
| H  | 32 | 2.912  | -5.068 | 2.625  |
| H  | 33 | 2.662  | -5.377 | 5.091  |
| H  | 34 | 1.771  | -3.504 | 6.487  |
| H  | 35 | 1.124  | -1.340 | 5.406  |
| H  | 36 | 4.084  | 2.801  | -0.901 |
| H  | 37 | 5.948  | 4.339  | -0.285 |
| H  | 38 | 5.703  | 6.804  | -0.623 |
| H  | 39 | 3.573  | 7.718  | -1.557 |
| H  | 40 | 1.707  | 6.185  | -2.147 |
| H  | 41 | -4.262 | 3.578  | 1.362  |
| H  | 42 | -6.458 | 3.215  | 2.496  |
| H  | 43 | -7.549 | 0.969  | 2.428  |
| H  | 44 | -6.426 | -0.910 | 1.225  |
| H  | 45 | -4.232 | -0.553 | 0.110  |
| H  | 46 | -0.596 | -1.959 | -4.708 |
| H  | 47 | -1.935 | -3.698 | -5.901 |
| H  | 48 | -2.088 | -6.015 | -4.975 |
| H  | 49 | -0.900 | -6.577 | -2.854 |
| H  | 50 | 0.441  | -4.830 | -1.666 |
| O  | 51 | 1.318  | -0.793 | 2.892  |
| O  | 52 | 1.769  | 3.498  | -1.888 |

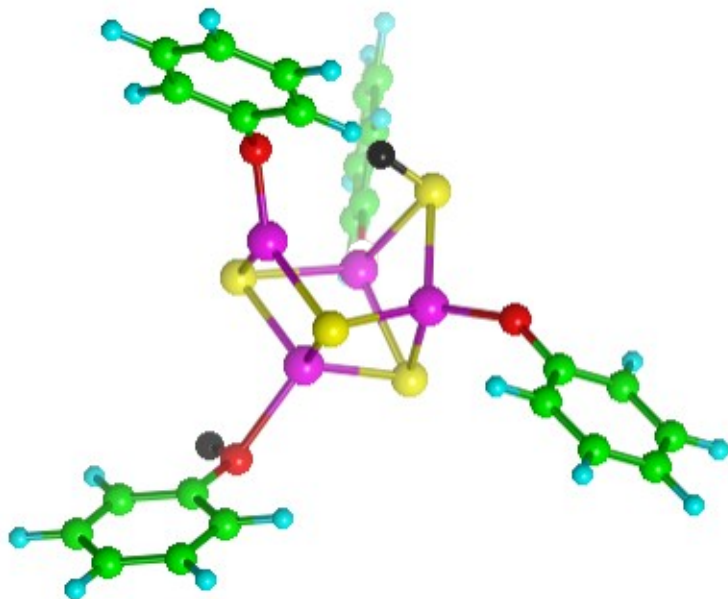
|   |    |        |        |        |        |
|---|----|--------|--------|--------|--------|
|   | O  | 53     | -2.921 | 1.778  | 0.040  |
|   | O  | 54     | 0.766  | -2.363 | -2.483 |
|   | S  | 55     | 0.532  | 2.403  | 1.409  |
|   | S  | 56     | 2.414  | 0.016  | -0.427 |
|   | S  | 57     | -0.925 | -1.198 | 0.367  |
|   | S  | 58     | -0.415 | 1.018  | -2.512 |
| <hr/>   |    |        |        |        |        |
|  <p>[Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>3</sub>(HSEt)]<sup>0</sup>, isomer C<sup>ex</sup> {opp / S=0}<br/>fe4s3shset4hox.car_8</p> | 42 |        |        |        |        |
|   | C  | 1      | 4.365  | -2.299 | 2.615  |
|   | C  | 2      | 3.340  | -1.645 | 3.546  |
|   | C  | 3      | 3.400  | 2.074  | -3.764 |
|   | C  | 4      | 2.750  | 0.699  | -3.582 |
|   | C  | 5      | -2.943 | 4.420  | -0.183 |
|   | C  | 6      | -3.688 | 3.636  | 0.900  |
|   | C  | 7      | -4.169 | -3.069 | -1.070 |
|   | C  | 8      | -3.415 | -3.582 | 0.158  |
|   | H  | 9      | 2.712  | 2.082  | 0.120  |
|   | H  | 10     | -1.180 | -4.179 | 0.972  |
|   | Fe | 11     | 1.256  | 0.073  | 1.556  |
|   | Fe | 12     | 0.543  | 0.554  | -1.089 |
|   | Fe | 13     | -1.696 | 0.983  | 1.228  |
|   | Fe | 14     | -0.738 | -1.325 | 0.396  |
|   | H  | 15     | 5.294  | -1.715 | 2.577  |
|   | H  | 16     | 3.304  | 2.685  | -2.858 |
|   | H  | 17     | 2.936  | 2.625  | -4.592 |
|   | H  | 18     | -2.269 | 5.164  | 0.260  |
|   | H  | 19     | -3.973 | -3.692 | -1.952 |
|   | H  | 20     | -5.248 | -3.098 | -0.866 |
|   | H  | 21     | 2.410  | -2.222 | 3.595  |
|   | H  | 22     | 3.736  | -1.559 | 4.566  |
|   | H  | 23     | 4.472  | 1.956  | -3.989 |
|   | H  | 24     | 2.859  | 0.091  | -4.489 |
|   | H  | 25     | 3.203  | 0.144  | -2.754 |
|   | H  | 26     | -3.667 | 4.948  | -0.824 |
|   | H  | 27     | -4.310 | 4.304  | 1.510  |
|   | H  | 28     | -4.339 | 2.870  | 0.467  |
|   | H  | 29     | -3.897 | -2.033 | -1.307 |
|   | H  | 30     | -3.591 | -2.960 | 1.040  |
|   | H  | 31     | -3.673 | -4.622 | 0.386  |
|   | H  | 32     | -2.347 | 3.752  | -0.817 |
|   | H  | 33     | 4.609  | -3.310 | 2.977  |
|   | H  | 34     | 3.972  | -2.387 | 1.594  |
|   | S  | 35     | 2.911  | 0.120  | 3.069  |
|   | S  | 36     | 0.895  | 0.803  | -3.295 |
|   | S  | 37     | -2.557 | 2.801  | 2.151  |
|   | S  | 38     | -1.559 | -3.580 | -0.188 |
|   | S  | 39     | -1.805 | 0.299  | -0.873 |
|   | S  | 40     | 1.394  | 2.201  | 0.439  |
|   | S  | 41     | 1.498  | -1.380 | -0.154 |
| S   | 42 | -0.795 | -0.627 | 2.524  |        |



[Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>3</sub>(HOPh)]<sup>0</sup>, isomer C<sup>ex</sup> {opp / S=0}  
 fe4s3shoph4hox.car\_6

| 58 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | -2.357 | 3.399  | 1.884  |
| C  | 2  | -1.336 | 3.511  | 2.855  |
| C  | 3  | -1.545 | 4.279  | 4.004  |
| C  | 4  | -2.762 | 4.950  | 4.206  |
| C  | 5  | -3.774 | 4.846  | 3.238  |
| C  | 6  | -3.580 | 4.081  | 2.084  |
| C  | 7  | 1.031  | 1.362  | -5.020 |
| C  | 8  | 1.053  | 2.758  | -4.781 |
| C  | 9  | 1.074  | 3.652  | -5.856 |
| C  | 10 | 1.067  | 3.180  | -7.179 |
| C  | 11 | 1.035  | 1.797  | -7.419 |
| C  | 12 | 1.018  | 0.891  | -6.355 |
| C  | 13 | -2.721 | -3.751 | -0.027 |
| C  | 14 | -4.091 | -3.837 | -0.292 |
| C  | 15 | -4.919 | -4.481 | 0.639  |
| C  | 16 | -4.380 | -5.020 | 1.814  |
| C  | 17 | -3.001 | -4.924 | 2.054  |
| C  | 18 | -2.160 | -4.290 | 1.132  |
| C  | 19 | 3.999  | -1.124 | 2.123  |
| C  | 20 | 5.265  | -1.438 | 1.574  |
| C  | 21 | 6.132  | -2.290 | 2.261  |
| C  | 22 | 5.759  | -2.844 | 3.498  |
| C  | 23 | 4.502  | -2.534 | 4.043  |
| C  | 24 | 3.623  | -1.683 | 3.368  |
| H  | 25 | 2.949  | 1.851  | -1.271 |
| H  | 26 | -2.336 | -2.864 | -1.748 |
| Fe | 27 | -1.532 | 1.045  | 0.257  |
| Fe | 28 | 0.668  | 0.323  | -2.203 |
| Fe | 29 | -0.590 | -1.346 | -0.461 |
| Fe | 30 | 1.677  | -0.152 | 0.416  |
| H  | 31 | -0.391 | 2.995  | 2.691  |
| H  | 32 | -0.749 | 4.359  | 4.745  |
| H  | 33 | -2.919 | 5.547  | 5.103  |
| H  | 34 | -4.721 | 5.368  | 3.381  |
| H  | 35 | -4.356 | 3.994  | 1.325  |
| H  | 36 | 1.060  | 3.120  | -3.754 |
| H  | 37 | 1.099  | 4.724  | -5.659 |
| H  | 38 | 1.082  | 3.882  | -8.012 |
| H  | 39 | 1.025  | 1.422  | -8.442 |
| H  | 40 | 0.998  | -0.185 | -6.525 |
| H  | 41 | -4.509 | -3.401 | -1.199 |
| H  | 42 | -5.988 | -4.550 | 0.442  |
| H  | 43 | -5.029 | -5.510 | 2.537  |
| H  | 44 | -2.575 | -5.343 | 2.965  |
| H  | 45 | -1.088 | -4.211 | 1.306  |
| H  | 46 | 5.543  | -1.002 | 0.616  |
| H  | 47 | 7.105  | -2.525 | 1.831  |
| H  | 48 | 6.439  | -3.507 | 4.031  |
| H  | 49 | 4.207  | -2.957 | 5.004  |
| H  | 50 | 2.650  | -1.430 | 3.786  |
| O  | 51 | -2.183 | 2.681  | 0.748  |
| O  | 52 | 1.049  | 0.463  | -4.014 |

|   |    |    |        |        |        |
|---|----|----|--------|--------|--------|
|   | O  | 53 | -1.848 | -3.097 | -0.934 |
|   | O  | 54 | 3.180  | -0.266 | 1.480  |
|   | S  | 55 | -1.680 | 0.206  | -1.814 |
|   | S  | 56 | 1.687  | 1.968  | -0.770 |
|   | S  | 57 | -0.382 | -0.427 | 1.561  |
|   | S  | 58 | 1.528  | -1.664 | -1.269 |
|   |    | 42 |        |        |        |
|  <p>[Fe<sub>4</sub>S<sub>3</sub>(SH)(SEt)<sub>3</sub>(HSEt)]<sup>0</sup>, isomer C<sup>en</sup> {opp / S=0}<br/>fe4s3shset4hon.car_6</p> | C  | 1  | 4.791  | -1.609 | 2.526  |
|   | C  | 2  | 3.692  | -1.078 | 3.452  |
|   | C  | 3  | 3.044  | 2.400  | -3.668 |
|   | C  | 4  | 2.649  | 0.920  | -3.659 |
|   | C  | 5  | -3.463 | 3.944  | -0.482 |
|   | C  | 6  | -3.892 | 3.167  | 0.765  |
|   | C  | 7  | -3.872 | -3.628 | -0.701 |
|   | C  | 8  | -2.964 | -4.027 | 0.463  |
|   | H  | 9  | 0.036  | 2.915  | 0.465  |
|   | H  | 10 | -0.603 | -4.296 | 1.097  |
|   | Fe | 11 | 1.310  | 0.174  | 1.491  |
|   | Fe | 12 | 0.505  | 0.462  | -1.194 |
|   | Fe | 13 | -1.358 | 1.003  | 1.038  |
|   | Fe | 14 | -0.564 | -1.444 | 0.427  |
|   | H  | 15 | 5.619  | -0.893 | 2.445  |
|   | H  | 16 | 2.831  | 2.874  | -2.701 |
|   | H  | 17 | 2.501  | 2.952  | -4.446 |
|   | H  | 18 | -2.914 | 4.856  | -0.213 |
|   | H  | 19 | -3.676 | -4.240 | -1.591 |
|   | H  | 20 | -4.920 | -3.781 | -0.407 |
|   | H  | 21 | 2.861  | -1.787 | 3.542  |
|   | H  | 22 | 4.083  | -0.893 | 4.460  |
|   | H  | 23 | 4.122  | 2.496  | -3.869 |
|   | H  | 24 | 2.868  | 0.448  | -4.626 |
|   | H  | 25 | 3.189  | 0.362  | -2.886 |
|   | H  | 26 | -4.352 | 4.240  | -1.062 |
|   | H  | 27 | -4.563 | 3.770  | 1.391  |
|   | H  | 28 | -4.416 | 2.242  | 0.501  |
|   | H  | 29 | -3.744 | -2.572 | -0.967 |
|   | H  | 30 | -3.150 | -3.425 | 1.357  |
|   | H  | 31 | -3.062 | -5.089 | 0.709  |
|   | H  | 32 | -2.824 | 3.333  | -1.131 |
|   | H  | 33 | 5.193  | -2.554 | 2.925  |
|   | H  | 34 | 4.402  | -1.797 | 1.518  |
|   | S  | 35 | 2.995  | 0.580  | 2.909  |
|   | S  | 36 | 0.806  | 0.639  | -3.409 |
|   | S  | 37 | -2.478 | 2.720  | 1.921  |
|   | S  | 38 | -1.157 | -3.782 | -0.032 |
|   | S  | 39 | -1.774 | 0.021  | -0.910 |
|   | S  | 40 | 1.217  | 2.262  | 0.226  |
|   | S  | 41 | 1.679  | -1.289 | -0.171 |
|   | S  | 42 | -0.647 | -0.598 | 2.498  |

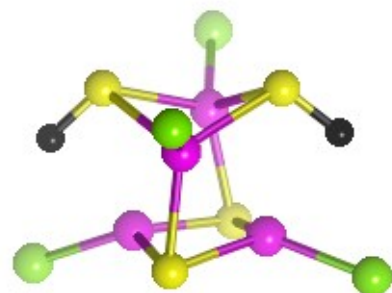


[Fe<sub>4</sub>S<sub>3</sub>(SH)(OPh)<sub>3</sub>(HOPh)]<sup>0</sup>, isomer C<sup>en</sup> {opp / S=0}  
fe4s3shoph4hon.car\_4

| 58 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | -1.781 | 3.340  | 2.318  |
| C  | 2  | -0.743 | 3.472  | 3.266  |
| C  | 3  | -0.980 | 4.134  | 4.476  |
| C  | 4  | -2.246 | 4.672  | 4.760  |
| C  | 5  | -3.277 | 4.543  | 3.816  |
| C  | 6  | -3.054 | 3.883  | 2.603  |
| C  | 7  | 0.476  | 1.726  | -4.993 |
| C  | 8  | 0.680  | 3.079  | -4.628 |
| C  | 9  | 0.728  | 4.072  | -5.610 |
| C  | 10 | 0.574  | 3.745  | -6.967 |
| C  | 11 | 0.371  | 2.404  | -7.333 |
| C  | 12 | 0.322  | 1.400  | -6.363 |
| C  | 13 | -2.767 | -3.760 | -0.020 |
| C  | 14 | -4.145 | -3.853 | -0.234 |
| C  | 15 | -4.934 | -4.513 | 0.719  |
| C  | 16 | -4.348 | -5.062 | 1.867  |
| C  | 17 | -2.962 | -4.958 | 2.058  |
| C  | 18 | -2.159 | -4.309 | 1.111  |
| C  | 19 | 4.159  | -1.396 | 1.558  |
| C  | 20 | 5.342  | -1.732 | 0.857  |
| C  | 21 | 6.238  | -2.654 | 1.403  |
| C  | 22 | 5.976  | -3.255 | 2.645  |
| C  | 23 | 4.802  | -2.924 | 3.341  |
| C  | 24 | 3.895  | -2.003 | 2.808  |
| H  | 25 | 0.815  | 2.636  | -0.266 |
| H  | 26 | -2.449 | -2.855 | -1.745 |
| Fe | 27 | -1.358 | 1.008  | 0.535  |
| Fe | 28 | 0.388  | 0.486  | -2.240 |
| Fe | 29 | -0.653 | -1.345 | -0.493 |
| Fe | 30 | 1.710  | -0.231 | 0.189  |
| H  | 31 | 0.237  | 3.053  | 3.040  |
| H  | 32 | -0.171 | 4.234  | 5.199  |
| H  | 33 | -2.424 | 5.187  | 5.703  |
| H  | 34 | -4.261 | 4.965  | 4.023  |
| H  | 35 | -3.845 | 3.785  | 1.859  |
| H  | 36 | 0.809  | 3.331  | -3.577 |
| H  | 37 | 0.889  | 5.108  | -5.314 |
| H  | 38 | 0.612  | 4.524  | -7.726 |
| H  | 39 | 0.251  | 2.141  | -8.384 |
| H  | 40 | 0.168  | 0.356  | -6.634 |
| H  | 41 | -4.601 | -3.411 | -1.120 |
| H  | 42 | -6.010 | -4.583 | 0.561  |
| H  | 43 | -4.966 | -5.565 | 2.608  |
| H  | 44 | -2.498 | -5.383 | 2.946  |
| H  | 45 | -1.082 | -4.226 | 1.248  |
| H  | 46 | 5.535  | -1.253 | -0.102 |
| H  | 47 | 7.148  | -2.904 | 0.857  |
| H  | 48 | 6.680  | -3.971 | 3.067  |
| H  | 49 | 4.592  | -3.385 | 4.306  |
| H  | 50 | 2.985  | -1.733 | 3.342  |
| O  | 51 | -1.561 | 2.735  | 1.121  |
| O  | 52 | 0.432  | 0.733  | -4.081 |

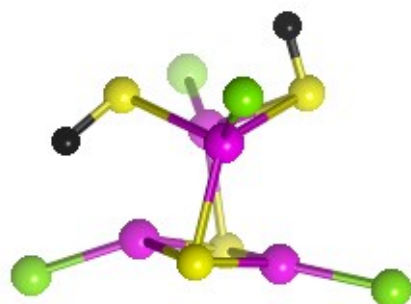
|   |    |        |        |        |
|---|----|--------|--------|--------|
| O | 53 | -1.930 | -3.088 | -0.950 |
| O | 54 | 3.320  | -0.469 | 1.053  |
| S | 55 | -1.886 | 0.329  | -1.530 |
| S | 56 | 1.784  | 1.945  | -0.922 |
| S | 57 | -0.167 | -0.633 | 1.570  |
| S | 58 | 1.341  | -1.575 | -1.599 |

**Table S4.** Examples of doubly-protonated  $[\text{Fe}_4\text{S}_2(\text{SH})_2\text{X}_4]^0$  (added protons are coloured black).



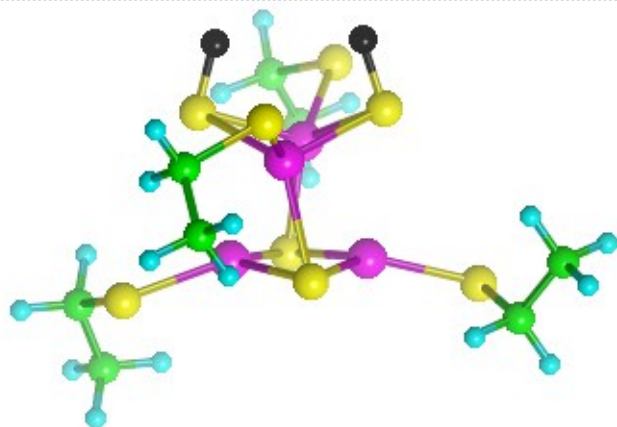
*endo, endo*  $[\text{Fe}_4\text{S}_2(\text{SH})_2\text{Cl}_4]^0$   
fe4s2sh2cl4nn.car\_2

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 14 |    |        |        |        |
| Cl | 1  | 0.186  | 2.762  | -2.734 |
| Cl | 2  | -3.214 | -1.600 | -1.557 |
| Cl | 3  | -0.599 | 0.938  | 3.843  |
| Cl | 4  | 3.172  | -1.867 | 0.721  |
| H  | 5  | -2.873 | 0.766  | -0.078 |
| H  | 6  | 2.562  | 0.866  | 0.623  |
| Fe | 7  | 0.115  | 1.306  | -1.122 |
| Fe | 8  | -1.333 | -0.998 | -0.640 |
| Fe | 9  | -0.436 | 0.506  | 1.719  |
| Fe | 10 | 1.211  | -1.086 | 0.184  |
| S  | 11 | 0.564  | -0.797 | -1.928 |
| S  | 12 | -1.896 | 1.677  | 0.213  |
| S  | 13 | 1.491  | 1.698  | 0.805  |
| S  | 14 | -0.661 | -1.751 | 1.346  |



*endo, exo*  $[\text{Fe}_4\text{S}_2(\text{SH})_2\text{Cl}_4]^0$   
fe4s2sh2cl4nxa.car\_2

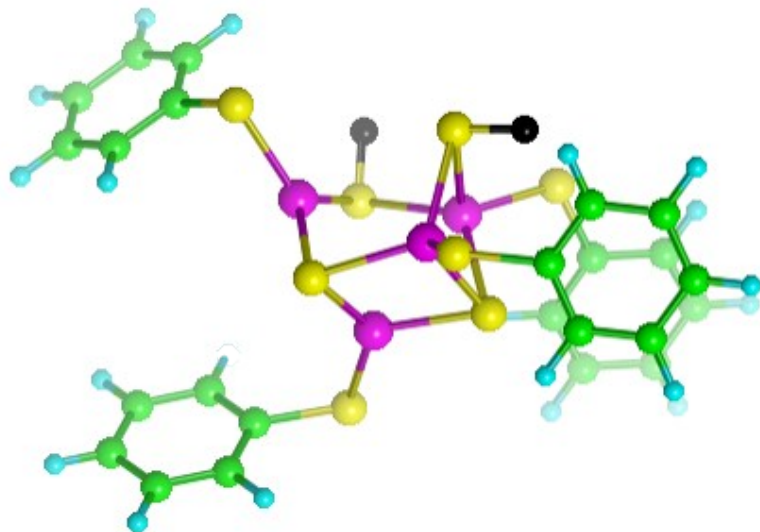
|    |    |        |        |        |
|----|----|--------|--------|--------|
| 14 |    |        |        |        |
| Cl | 1  | -0.528 | 2.197  | -3.205 |
| Cl | 2  | -3.443 | -1.605 | -0.484 |
| Cl | 3  | 0.538  | 1.746  | 3.506  |
| Cl | 4  | 3.302  | -1.862 | 0.494  |
| H  | 5  | -2.780 | 0.920  | 0.540  |
| H  | 6  | 1.354  | 3.101  | 0.217  |
| Fe | 7  | -0.131 | 1.115  | -1.362 |
| Fe | 8  | -1.406 | -0.932 | -0.100 |
| Fe | 9  | 0.155  | 0.874  | 1.549  |
| Fe | 10 | 1.212  | -1.396 | 0.210  |
| S  | 11 | 0.190  | -1.154 | -1.750 |
| S  | 12 | -1.743 | 1.792  | 0.347  |
| S  | 13 | 1.722  | 1.810  | -0.019 |
| S  | 14 | -0.383 | -1.375 | 1.840  |



*exo,exo* [Fe<sub>4</sub>S<sub>2</sub>(SH)<sub>2</sub>(SEt)<sub>4</sub>]<sup>0</sup>  
 fe4s2sh2set4xxpb.car\_4

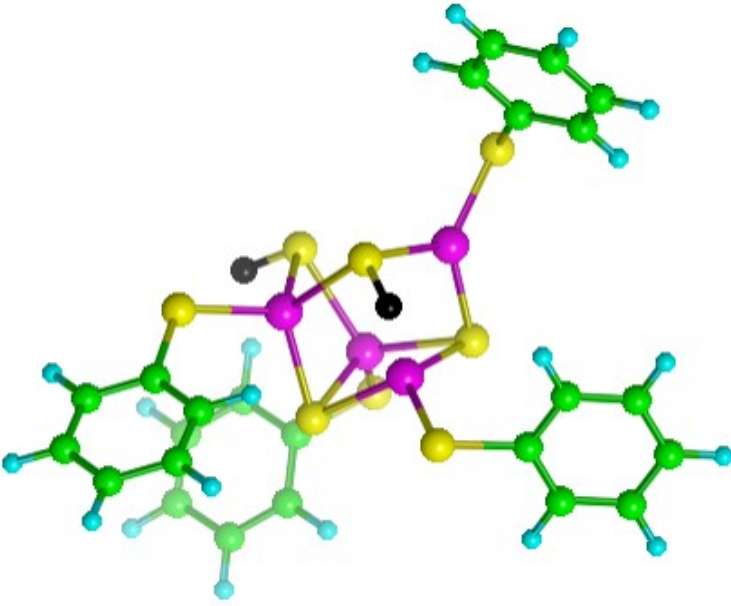
|    |    |        |        |        |
|----|----|--------|--------|--------|
| 42 |    |        |        |        |
| C  | 1  | -1.569 | -0.387 | 5.022  |
| C  | 2  | -1.874 | 0.865  | 4.214  |
| C  | 3  | 5.291  | -0.879 | 1.684  |
| C  | 4  | 4.441  | -1.923 | 0.975  |
| C  | 5  | 0.321  | 1.717  | -5.063 |
| C  | 6  | -0.218 | 2.639  | -3.979 |
| C  | 7  | -3.369 | -2.868 | -2.153 |
| C  | 8  | -3.844 | -1.693 | -1.312 |
| H  | 9  | -1.284 | 3.231  | 0.448  |
| H  | 10 | 1.521  | 3.290  | 0.674  |
| Fe | 11 | 0.033  | 1.012  | 1.590  |
| Fe | 12 | 1.611  | -0.801 | -0.202 |
| Fe | 13 | 0.380  | 1.401  | -1.043 |
| Fe | 14 | -0.981 | -0.860 | 0.035  |
| H  | 15 | -0.943 | -0.154 | 5.894  |
| H  | 16 | 4.688  | -0.010 | 1.978  |
| H  | 17 | 6.106  | -0.523 | 1.038  |
| H  | 18 | 1.270  | 2.096  | -5.469 |
| H  | 19 | -3.510 | -3.819 | -1.620 |
| H  | 20 | -3.938 | -2.915 | -3.096 |
| H  | 21 | -2.500 | 0.641  | 3.340  |
| H  | 22 | -2.409 | 1.610  | 4.820  |
| H  | 23 | 5.737  | -1.315 | 2.593  |
| H  | 24 | 5.045  | -2.791 | 0.675  |
| H  | 25 | 3.627  | -2.285 | 1.615  |
| H  | 26 | -0.404 | 1.642  | -5.890 |
| H  | 27 | -0.394 | 3.652  | -4.371 |
| H  | 28 | -1.172 | 2.275  | -3.574 |
| H  | 29 | -2.303 | -2.771 | -2.403 |
| H  | 30 | -3.687 | -0.734 | -1.823 |
| H  | 31 | -4.916 | -1.779 | -1.083 |
| H  | 32 | 0.499  | 0.707  | -4.669 |
| H  | 33 | -2.509 | -0.839 | 5.380  |
| H  | 34 | -1.040 | -1.134 | 4.414  |
| S  | 35 | -0.341 | 1.735  | 3.637  |
| S  | 36 | 3.713  | -1.275 | -0.607 |
| S  | 37 | 0.980  | 2.872  | -2.583 |
| S  | 38 | -3.024 | -1.606 | 0.351  |
| S  | 39 | 0.097  | -0.713 | -1.880 |
| S  | 40 | -1.596 | 1.937  | 0.148  |
| S  | 41 | 0.525  | -1.241 | 1.661  |
| S  | 42 | 1.940  | 1.992  | 0.634  |





*exo,exo* [Fe<sub>4</sub>S<sub>2</sub>(SH)<sub>2</sub>(SPh)<sub>4</sub>]<sup>0</sup>  
 fe4s2sh2sph4cx.car\_4

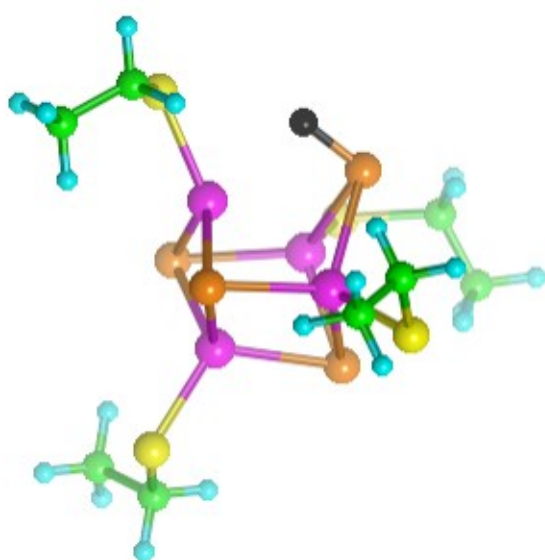
| 58 |    |        |        |        |
|----|----|--------|--------|--------|
| C  | 1  | 3.840  | 0.216  | -2.412 |
| C  | 2  | 3.069  | -0.881 | -2.848 |
| C  | 3  | 3.660  | -1.894 | -3.613 |
| C  | 4  | 5.018  | -1.825 | -3.960 |
| C  | 5  | 5.785  | -0.731 | -3.534 |
| C  | 6  | 5.205  | 0.284  | -2.765 |
| C  | 7  | -4.133 | 3.166  | -0.412 |
| C  | 8  | -5.278 | 2.344  | -0.390 |
| C  | 9  | -6.204 | 2.399  | -1.439 |
| C  | 10 | -6.005 | 3.276  | -2.516 |
| C  | 11 | -4.871 | 4.101  | -2.536 |
| C  | 12 | -3.937 | 4.049  | -1.494 |
| C  | 13 | 2.995  | 0.103  | 4.704  |
| C  | 14 | 3.816  | 1.227  | 4.920  |
| C  | 15 | 5.199  | 1.066  | 5.076  |
| C  | 16 | 5.775  | -0.211 | 5.019  |
| C  | 17 | 4.957  | -1.333 | 4.809  |
| C  | 18 | 3.574  | -1.180 | 4.653  |
| C  | 19 | -2.616 | -2.971 | -0.864 |
| C  | 20 | -3.500 | -2.344 | -1.761 |
| C  | 21 | -4.871 | -2.630 | -1.708 |
| C  | 22 | -5.369 | -3.540 | -0.765 |
| C  | 23 | -4.487 | -4.169 | 0.125  |
| C  | 24 | -3.115 | -3.888 | 0.080  |
| H  | 25 | -0.543 | 2.633  | -1.787 |
| H  | 26 | 2.530  | 2.659  | 1.877  |
| Fe | 27 | 1.360  | 1.046  | -0.224 |
| Fe | 28 | -1.774 | 1.328  | 0.436  |
| Fe | 29 | 0.675  | 0.507  | 2.412  |
| Fe | 30 | -0.342 | -1.179 | 0.586  |
| H  | 31 | 2.013  | -0.941 | -2.598 |
| H  | 32 | 3.053  | -2.737 | -3.940 |
| H  | 33 | 5.472  | -2.615 | -4.557 |
| H  | 34 | 6.840  | -0.665 | -3.799 |
| H  | 35 | 5.804  | 1.130  | -2.431 |
| H  | 36 | -5.441 | 1.673  | 0.451  |
| H  | 37 | -7.085 | 1.759  | -1.411 |
| H  | 38 | -6.728 | 3.317  | -3.329 |
| H  | 39 | -4.711 | 4.789  | -3.366 |
| H  | 40 | -3.060 | 4.694  | -1.510 |
| H  | 41 | 3.368  | 2.219  | 4.975  |
| H  | 42 | 5.826  | 1.941  | 5.245  |
| H  | 43 | 6.850  | -0.334 | 5.143  |
| H  | 44 | 5.394  | -2.330 | 4.767  |
| H  | 45 | 2.939  | -2.049 | 4.492  |
| H  | 46 | -3.114 | -1.638 | -2.495 |
| H  | 47 | -5.547 | -2.139 | -2.407 |
| H  | 48 | -6.436 | -3.760 | -0.726 |
| H  | 49 | -4.865 | -4.882 | 0.858  |
| H  | 50 | -2.432 | -4.381 | 0.769  |
| S  | 51 | 1.216  | 2.672  | 1.519  |
| S  | 52 | 3.163  | 1.587  | -1.468 |

|   |    |    |        |        |        |
|---|----|----|--------|--------|--------|
|   | S  | 53 | -0.624 | 1.287  | -1.584 |
|   | S  | 54 | -2.967 | 3.154  | 0.978  |
|   | S  | 55 | 1.839  | -0.847 | 1.008  |
|   | S  | 56 | 1.200  | 0.291  | 4.597  |
|   | S  | 57 | -1.546 | -0.162 | 2.148  |
|   | S  | 58 | -0.833 | -2.665 | -0.997 |
| <hr/>   |    |    |        |        |        |
|   |    | 58 |        |        |        |
|  | C  | 1  | -4.353 | -0.556 | 1.553  |
|   | C  | 2  | -3.462 | -1.201 | 2.434  |
|   | C  | 3  | -3.918 | -2.231 | 3.266  |
|   | C  | 4  | -5.265 | -2.623 | 3.240  |
|   | C  | 5  | -6.157 | -1.977 | 2.370  |
|   | C  | 6  | -5.708 | -0.952 | 1.531  |
|   | C  | 7  | 2.902  | 4.717  | 0.601  |
|   | C  | 8  | 4.175  | 4.469  | 1.152  |
|   | C  | 9  | 4.526  | 5.027  | 2.388  |
|   | C  | 10 | 3.616  | 5.839  | 3.082  |
|   | C  | 11 | 2.354  | 6.100  | 2.526  |
|   | C  | 12 | 1.995  | 5.544  | 1.292  |
|   | C  | 13 | -1.539 | -1.694 | -4.905 |
|   | C  | 14 | -2.564 | -1.004 | -5.580 |
|   | C  | 15 | -3.735 | -1.678 | -5.954 |
|   | C  | 16 | -3.891 | -3.041 | -5.662 |
|   | C  | 17 | -2.866 | -3.730 | -4.995 |
|   | C  | 18 | -1.694 | -3.064 | -4.618 |
|   | C  | 19 | 3.098  | -1.933 | 1.726  |
|   | C  | 20 | 3.865  | -0.937 | 2.359  |
|   | C  | 21 | 5.264  | -1.009 | 2.337  |
|   | C  | 22 | 5.909  | -2.074 | 1.691  |
|   | C  | 23 | 5.145  | -3.070 | 1.065  |
|   | C  | 24 | 3.746  | -3.005 | 1.082  |
|   | H  | 25 | 0.312  | 0.885  | 2.155  |
|   | H  | 26 | -2.571 | 1.589  | -2.880 |
|   | Fe | 27 | -1.771 | 0.756  | -0.276 |
|   | Fe | 28 | 1.550  | 2.109  | -0.326 |
|   | Fe | 29 | -0.151 | -0.013 | -2.431 |
|   | Fe | 30 | 0.649  | -0.537 | 0.125  |
|   | H  | 31 | -2.420 | -0.895 | 2.473  |
|   | H  | 32 | -3.218 | -2.722 | 3.942  |
|   | H  | 33 | -5.616 | -3.422 | 3.892  |
|   | H  | 34 | -7.205 | -2.274 | 2.343  |
|   | H  | 35 | -6.402 | -0.457 | 0.853  |
|   | H  | 36 | 4.883  | 3.847  | 0.607  |
|   | H  | 37 | 5.513  | 4.828  | 2.806  |
|   | H  | 38 | 3.888  | 6.270  | 4.044  |
|   | H  | 39 | 1.644  | 6.736  | 3.054  |
|   | H  | 40 | 1.017  | 5.747  | 0.860  |
|   | H  | 41 | -2.436 | 0.051  | -5.818 |
|   | H  | 42 | -4.521 | -1.137 | -6.479 |
|   | H  | 43 | -4.801 | -3.564 | -5.955 |
|   | H  | 44 | -2.979 | -4.790 | -4.768 |
|   | H  | 45 | -0.898 | -3.599 | -4.103 |

*exo, endo* [Fe<sub>4</sub>S<sub>2</sub>(SH)<sub>2</sub>(SPh)<sub>4</sub>]<sup>0</sup>  
fe4s2sh2sph4bx.car\_3

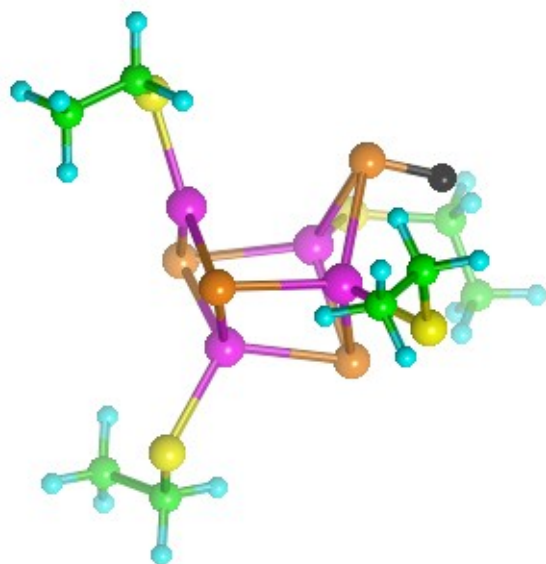
|   |    |        |        |        |
|---|----|--------|--------|--------|
| H | 46 | 3.368  | -0.113 | 2.867  |
| H | 47 | 5.849  | -0.232 | 2.829  |
| H | 48 | 6.998  | -2.127 | 1.678  |
| H | 49 | 5.637  | -3.902 | 0.563  |
| H | 50 | 3.154  | -3.778 | 0.596  |
| S | 51 | -1.456 | 2.037  | -2.241 |
| S | 52 | -3.874 | 0.817  | 0.498  |
| S | 53 | -0.144 | 1.836  | 1.288  |
| S | 54 | 2.469  | 4.025  | -1.020 |
| S | 55 | -1.192 | -1.347 | -0.946 |
| S | 56 | 0.012  | -0.850 | -4.511 |
| S | 57 | 1.983  | 0.210  | -1.503 |
| S | 58 | 1.287  | -1.902 | 1.807  |

**Table S5.** Examples of  $[\text{Fe}_4\text{Q}_3(\text{QH})_2(\text{SEt})_4]^-$ , Q = Se, Te (added protons are coloured black).



*endo*  $[\text{Fe}_4\text{Se}_3(\text{SeH})(\text{SEt})_4]^-$  {opp / S=0}  
fe4se3sehset4n.car\_3

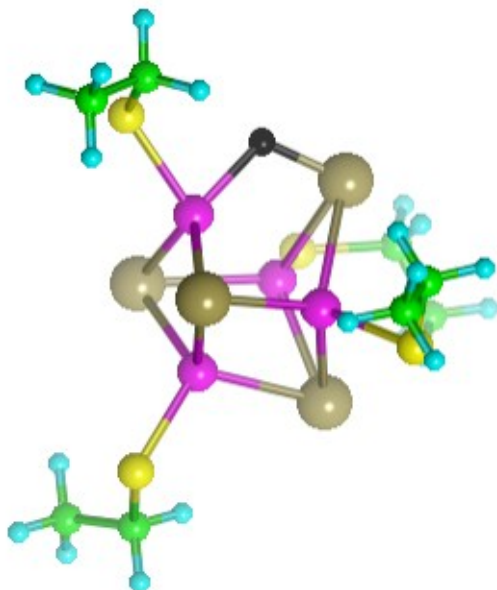
|    |    |        |        |        |
|----|----|--------|--------|--------|
| 41 |    |        |        |        |
| C  | 1  | 3.963  | -0.164 | -4.050 |
| C  | 2  | 3.251  | 1.186  | -3.912 |
| C  | 3  | -3.157 | -3.596 | -2.887 |
| C  | 4  | -2.114 | -4.122 | -1.894 |
| C  | 5  | -3.840 | 2.915  | 2.429  |
| C  | 6  | -2.524 | 3.637  | 2.119  |
| C  | 7  | 1.729  | -0.715 | 5.039  |
| C  | 8  | 2.539  | -0.027 | 3.934  |
| H  | 9  | 0.689  | 2.919  | 0.325  |
| Fe | 10 | 0.719  | 0.453  | -1.850 |
| Fe | 11 | -0.965 | -1.356 | -0.453 |
| Fe | 12 | -1.104 | 1.419  | 0.038  |
| Fe | 13 | 1.215  | -0.248 | 0.923  |
| H  | 14 | 3.681  | -0.666 | -4.986 |
| H  | 15 | -2.984 | -2.536 | -3.111 |
| H  | 16 | -4.173 | -3.694 | -2.480 |
| H  | 17 | -4.653 | 3.281  | 1.787  |
| H  | 18 | 2.188  | -1.672 | 5.325  |
| H  | 19 | 1.676  | -0.074 | 5.936  |
| H  | 20 | 3.549  | 1.698  | -2.989 |
| H  | 21 | 3.509  | 1.844  | -4.754 |
| H  | 22 | -3.104 | -4.163 | -3.833 |
| H  | 23 | -2.290 | -5.185 | -1.678 |
| H  | 24 | -1.100 | -4.028 | -2.300 |
| H  | 25 | -4.128 | 3.078  | 3.481  |
| H  | 26 | -2.623 | 4.715  | 2.301  |
| H  | 27 | -1.711 | 3.261  | 2.751  |
| H  | 28 | 0.706  | -0.920 | 4.702  |
| H  | 29 | 2.086  | 0.931  | 3.655  |
| H  | 30 | 3.564  | 0.178  | 4.271  |
| H  | 31 | -3.738 | 1.835  | 2.265  |
| H  | 32 | 5.057  | -0.020 | -4.051 |
| H  | 33 | 3.705  | -0.831 | -3.218 |
| S  | 34 | 1.377  | 1.083  | -3.940 |
| S  | 35 | -2.164 | -3.272 | -0.219 |



*endo* [Fe<sub>4</sub>Se<sub>3</sub>(SeH)(SEt)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4se3sehset4x.car\_4

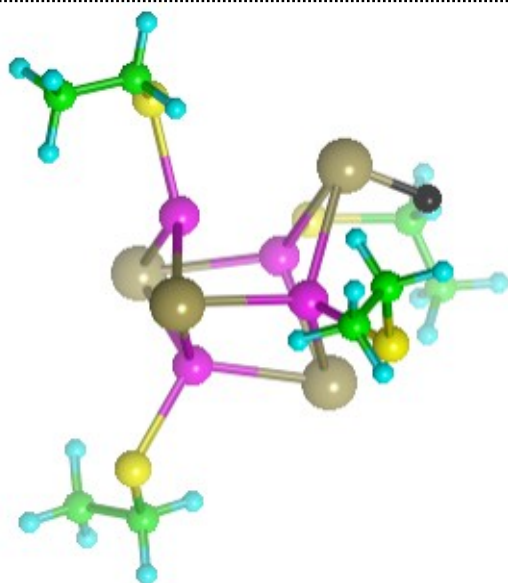
|    |    |        |        |        |
|----|----|--------|--------|--------|
| S  | 36 | -1.994 | 3.497  | 0.320  |
| S  | 37 | 2.718  | -1.094 | 2.398  |
| Se | 38 | -1.087 | -0.184 | 1.772  |
| Se | 39 | 1.835  | 2.020  | -0.081 |
| Se | 40 | 1.435  | -1.691 | -1.057 |
| Se | 41 | -1.736 | 0.307  | -2.030 |

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 41 |    |        |        |        |
| C  | 1  | 3.725  | -0.339 | -4.309 |
| C  | 2  | 3.196  | 1.056  | -3.957 |
| C  | 3  | -3.278 | -3.670 | -2.746 |
| C  | 4  | -2.107 | -4.116 | -1.861 |
| C  | 5  | -3.958 | 3.067  | 2.765  |
| C  | 6  | -2.655 | 3.689  | 2.253  |
| C  | 7  | 1.929  | -0.539 | 4.975  |
| C  | 8  | 2.702  | 0.124  | 3.829  |
| H  | 9  | 3.065  | 1.868  | -0.417 |
| Fe | 10 | 0.642  | 0.580  | -1.808 |
| Fe | 11 | -0.988 | -1.311 | -0.453 |
| Fe | 12 | -1.731 | 1.313  | 0.087  |
| Fe | 13 | 1.203  | -0.144 | 0.903  |
| H  | 14 | 3.332  | -0.677 | -5.278 |
| H  | 15 | -3.214 | -2.596 | -2.963 |
| H  | 16 | -4.239 | -3.857 | -2.247 |
| H  | 17 | -4.824 | 3.455  | 2.211  |
| H  | 18 | 2.380  | -1.504 | 5.247  |
| H  | 19 | 1.931  | 0.109  | 5.868  |
| H  | 20 | 3.592  | 1.396  | -2.993 |
| H  | 21 | 3.500  | 1.788  | -4.718 |
| H  | 22 | -3.271 | -4.218 | -3.703 |
| H  | 23 | -2.172 | -5.193 | -1.649 |
| H  | 24 | -1.146 | -3.933 | -2.355 |
| H  | 25 | -4.099 | 3.296  | 3.835  |
| H  | 26 | -2.662 | 4.777  | 2.397  |
| H  | 27 | -1.788 | 3.283  | 2.786  |
| H  | 28 | 0.886  | -0.724 | 4.686  |
| H  | 29 | 2.251  | 1.084  | 3.555  |
| H  | 30 | 3.743  | 0.317  | 4.122  |
| H  | 31 | -3.941 | 1.975  | 2.648  |
| H  | 32 | 4.826  | -0.328 | -4.367 |
| H  | 33 | 3.428  | -1.073 | -3.549 |
| S  | 34 | 1.324  | 1.163  | -3.901 |
| S  | 35 | -2.081 | -3.284 | -0.179 |
| S  | 36 | -2.372 | 3.445  | 0.411  |
| S  | 37 | 2.803  | -0.960 | 2.297  |
| Se | 38 | -1.138 | -0.208 | 1.783  |
| Se | 39 | 1.647  | 2.178  | -0.043 |
| Se | 40 | 1.380  | -1.585 | -1.081 |
| Se | 41 | -1.819 | 0.297  | -2.082 |



fe4te3tehset4n.car\_2

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 41 |    |        |        |        |
| C  | 1  | 3.259  | -0.441 | -4.866 |
| C  | 2  | 2.604  | 0.884  | -4.457 |
| C  | 3  | -3.630 | -4.254 | -2.039 |
| C  | 4  | -2.340 | -4.421 | -1.227 |
| C  | 5  | -3.162 | 3.639  | 3.137  |
| C  | 6  | -2.141 | 4.074  | 2.080  |
| C  | 7  | 2.757  | -0.338 | 4.767  |
| C  | 8  | 3.172  | 0.218  | 3.399  |
| H  | 9  | 0.083  | 2.850  | 0.041  |
| Fe | 10 | 0.368  | 0.254  | -2.028 |
| Fe | 11 | -1.156 | -1.480 | -0.187 |
| Fe | 12 | -1.219 | 1.461  | 0.153  |
| Fe | 13 | 1.178  | -0.287 | 0.773  |
| H  | 14 | 2.805  | -0.836 | -5.785 |
| H  | 15 | -3.743 | -3.219 | -2.386 |
| H  | 16 | -4.513 | -4.507 | -1.436 |
| H  | 17 | -4.183 | 3.908  | 2.833  |
| H  | 18 | 3.297  | -1.267 | 4.996  |
| H  | 19 | 2.976  | 0.395  | 5.563  |
| H  | 20 | 3.054  | 1.278  | -3.538 |
| H  | 21 | 2.742  | 1.640  | -5.244 |
| H  | 22 | -3.615 | -4.915 | -2.923 |
| H  | 23 | -2.229 | -5.460 | -0.885 |
| H  | 24 | -1.460 | -4.174 | -1.831 |
| H  | 25 | -2.947 | 4.128  | 4.102  |
| H  | 26 | -2.167 | 5.163  | 1.940  |
| H  | 27 | -1.125 | 3.799  | 2.381  |
| H  | 28 | 1.681  | -0.558 | 4.790  |
| H  | 29 | 2.616  | 1.131  | 3.160  |
| H  | 30 | 4.242  | 0.468  | 3.393  |
| H  | 31 | -3.127 | 2.553  | 3.285  |
| H  | 32 | 4.338  | -0.297 | -5.046 |
| H  | 33 | 3.140  | -1.195 | -4.078 |
| S  | 34 | 0.747  | 0.770  | -4.212 |
| S  | 35 | -2.302 | -3.376 | 0.334  |
| S  | 36 | -2.487 | 3.343  | 0.381  |
| S  | 37 | 2.940  | -1.020 | 2.004  |
| Te | 38 | -1.061 | -0.127 | 2.184  |
| Te | 39 | 1.643  | 2.119  | -0.402 |
| Te | 40 | 1.260  | -2.060 | -1.237 |
| Te | 41 | -2.295 | 0.158  | -1.891 |



*endo* [Fe<sub>4</sub>Te<sub>3</sub>(TeH)(SEt)<sub>4</sub>]<sup>-</sup> {opp / S=0}  
fe4te3tehset4s.car\_4

|    |    |        |        |        |
|----|----|--------|--------|--------|
| 41 |    |        |        |        |
| C  | 1  | 3.515  | -0.025 | -4.567 |
| C  | 2  | 2.938  | 1.260  | -3.963 |
| C  | 3  | -3.251 | -4.138 | -2.746 |
| C  | 4  | -2.072 | -4.354 | -1.789 |
| C  | 5  | -3.623 | 3.577  | 2.595  |
| C  | 6  | -2.199 | 3.905  | 2.128  |
| C  | 7  | 1.883  | -0.731 | 5.158  |
| C  | 8  | 2.498  | -0.014 | 3.950  |
| H  | 9  | 3.266  | 1.666  | -0.239 |
| Fe | 10 | 0.505  | 0.563  | -1.750 |
| Fe | 11 | -1.142 | -1.473 | -0.383 |
| Fe | 12 | -1.388 | 1.340  | 0.097  |
| Fe | 13 | 1.021  | -0.256 | 0.989  |
| H  | 14 | 3.106  | -0.208 | -5.570 |
| H  | 15 | -3.344 | -3.080 | -3.022 |
| H  | 16 | -4.197 | -4.452 | -2.284 |
| H  | 17 | -4.368 | 4.107  | 1.985  |
| H  | 18 | 2.441  | -1.646 | 5.402  |
| H  | 19 | 1.896  | -0.073 | 6.044  |
| H  | 20 | 3.350  | 1.445  | -2.965 |
| H  | 21 | 3.185  | 2.129  | -4.590 |
| H  | 22 | -3.108 | -4.726 | -3.670 |
| H  | 23 | -1.982 | -5.416 | -1.522 |
| H  | 24 | -1.129 | -4.045 | -2.253 |
| H  | 25 | -3.759 | 3.878  | 3.648  |
| H  | 26 | -1.996 | 4.979  | 2.233  |
| H  | 27 | -1.456 | 3.358  | 2.718  |
| H  | 28 | 0.842  | -1.016 | 4.955  |
| H  | 29 | 1.942  | 0.898  | 3.710  |
| H  | 30 | 3.537  | 0.276  | 4.160  |
| H  | 31 | -3.819 | 2.501  | 2.516  |
| H  | 32 | 4.613  | 0.047  | -4.650 |
| H  | 33 | 3.275  | -0.892 | -3.938 |
| S  | 34 | 1.064  | 1.250  | -3.851 |
| S  | 35 | -2.261 | -3.442 | -0.157 |
| S  | 36 | -1.907 | 3.528  | 0.310  |
| S  | 37 | 2.574  | -1.099 | 2.416  |
| Te | 38 | -1.421 | -0.314 | 2.064  |
| Te | 39 | 1.710  | 2.276  | 0.106  |
| Te | 40 | 1.415  | -1.811 | -1.143 |
| Te | 41 | -2.151 | 0.229  | -2.131 |

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