	Gaussian B3LYP Calculations, E(RT)			ADF BLYP
		Triple Zeta w/ polarization fcns on O & S		Basis Set IV
	LAN2LDZ	ECP = CEP	ECP = LANL2	with ZORA
$W_2(OH)_6$	-590.752025	-235.184324	-508.172222	-4.36768
$W(OH)_3$	-295.301315	-117.519616	-254.010883	-2.09344
$W_2(SH)_6$	-199.968303	-200.191419	-200.072262	-3.65408
$W(SH)_3$	-99.914132	-100.032857	-99.971065	-1.74715
$Mo_2(OH)_6$	-590.12601	-235.578447	-507.477386	-3.07233
$Mo(OH)_3$	-295.019027	-117.740137	-253.694298	-1.4691
$Mo_2(SH)_6$	-199.38608	-200.613858	-199.428936	-2.38526
$Mo(SH)_3$	-99.645981	-100.262776	-99.669782	-1.12925

Triple Bond Energies for Mo and W (Hartrees)				
$W_2(OH)_6$	0.149395	0.145092	0.150456	0.1808
$W_2(SH)_6$	0.140039	0.125705	0.130132	0.15978
$Mo_2(OH)_6$	0.087956	0.098173	0.08879	0.13413
$Mo_2(SH)_6$	0.094118	0.088306	0.089372	0.12676

Triple Bond Energies for Mo and W (kcal/mol)				
$W_2(OH)_6$	93.75	91.05	94.41	113.45
$W_2(SH)_6$	87.88	78.88	81.66	100.26
$Mo_2(OH)_6$	55.19	61.60	55.72	84.17
$Mo_2(SH)_6$	59.06	55.41	56.08	79.54

The bond strengths obtained using ADF are approximately 20 kcal/mol higher in energy than the CEP-121G calculations. This is due to the functional used. In the Gaussian calculations B3LYP was used, while for the ADF calculation BLYP was used. Gaussian calculations using BLYP with the CEP-121G basis set and CEP core potential gave a value of 110 kcal/mol for the W-W triple bond strength which is in close agreement with the ADF value.

Table 1: Metal-Metal bond strengths obtained from different computational methods

	Gaussian B3LYP Calculations, E(RT) Triple Zeta w/ polarization fcns on O & S			ADF BLYP Basis Set IV with ZORA
	LAN2LDZ	ECP = CEP	ECP = LANL2	
$W(OH)_3$	-295.301315	-117.519616	-254.010883	-2.09344
$W(SH)_3$	-99.914132	-100.032857	-99.971065	-1.74715
$Mo(OH)_3$	-295.019027	-117.740137	-253.694298	-1.4691
$Mo(SH)_3$	-99.645981	-100.262776	-99.669782	-1.12925
CMe	-77.728818	-12.835014	-61.627163	-0.77124
MeCCMe	-155.865105	-26.067368	-123.661209	-1.98328
$(HO)_3WCMe$	-373.31148	-130.626355	-315.906641	-3.17295
$(HS)_3WCMe$	-177.919287	-113.12811	-161.848004	-2.81314
$(HO)_3MoCMe$	-372.990201	-130.814197	-315.538869	-2.51763
$(HS)_3MoCMe$	-177.621263	-113.334528	-161.5158	-2.17176

M-C Bond Dissociation Energy (Hartrees)				
$(HO)_3WCMe$	0.281347	0.271725	0.268595	0.30827
$(HS)_3WCMe$	0.276337	0.260239	0.249776	0.29475
$(HO)_3MoCMe$	0.242356	0.239046	0.217408	0.27729
$(HS)_3MoCMe$	0.246464	0.236738	0.218855	0.27127

M-C Dissociation Energy (kcal/mol)				
$(HO)_3WCMe$	176.55	170.51	168.55	193.44
$(HS)_3WCMe$	173.40	163.30	156.74	184.96
$(HO)_3MoCMe$	152.08	150.00	136.43	174.00
$(HS)_3MoCMe$	154.66	148.56	137.33	170.22

C-C Dissociation Energy (Hartree and kcal/mol)				
MeCCMe	0.407469 255.69	0.39734 249.33	0.406883 255.32	0.4408 276.61

Table 2: M-C Bond Strengths obtained from different computational methods

	$W(OH)_3$	
	S=1/2	S=3/2
Spin Density		
W	0.99766	2.99072
O	0.00002	-0.02242
O	-0.0159	-0.02237
O	0.02223	-0.02241
H	-0.01591	0.02551
H	0.02971	0.02548
H	0.00221	0.02548
$<S^2>$	0.7554	3.75628
E(RT) (Hartree)	-117.514015	-117.519616

	$Mo(OH)_3$	
	S=1/2	S=3/2
Spin Density		
Mo	0.992376	2.987721
O	-0.015248	-0.015858
O	-0.000115	-0.016001
O	-0.015438	-0.015858
H	0.026909	0.020084
H	0.005811	0.019957
H	0.005705	0.019957
$<S^2>$	0.756343	3.759562
E(RT) (Hartree)	-117.715347	-117.740137

Table 3: Comparison of the Energy and Spin Density of $M(OH)_3$ fragments with 1 and 3 unpaired electrons

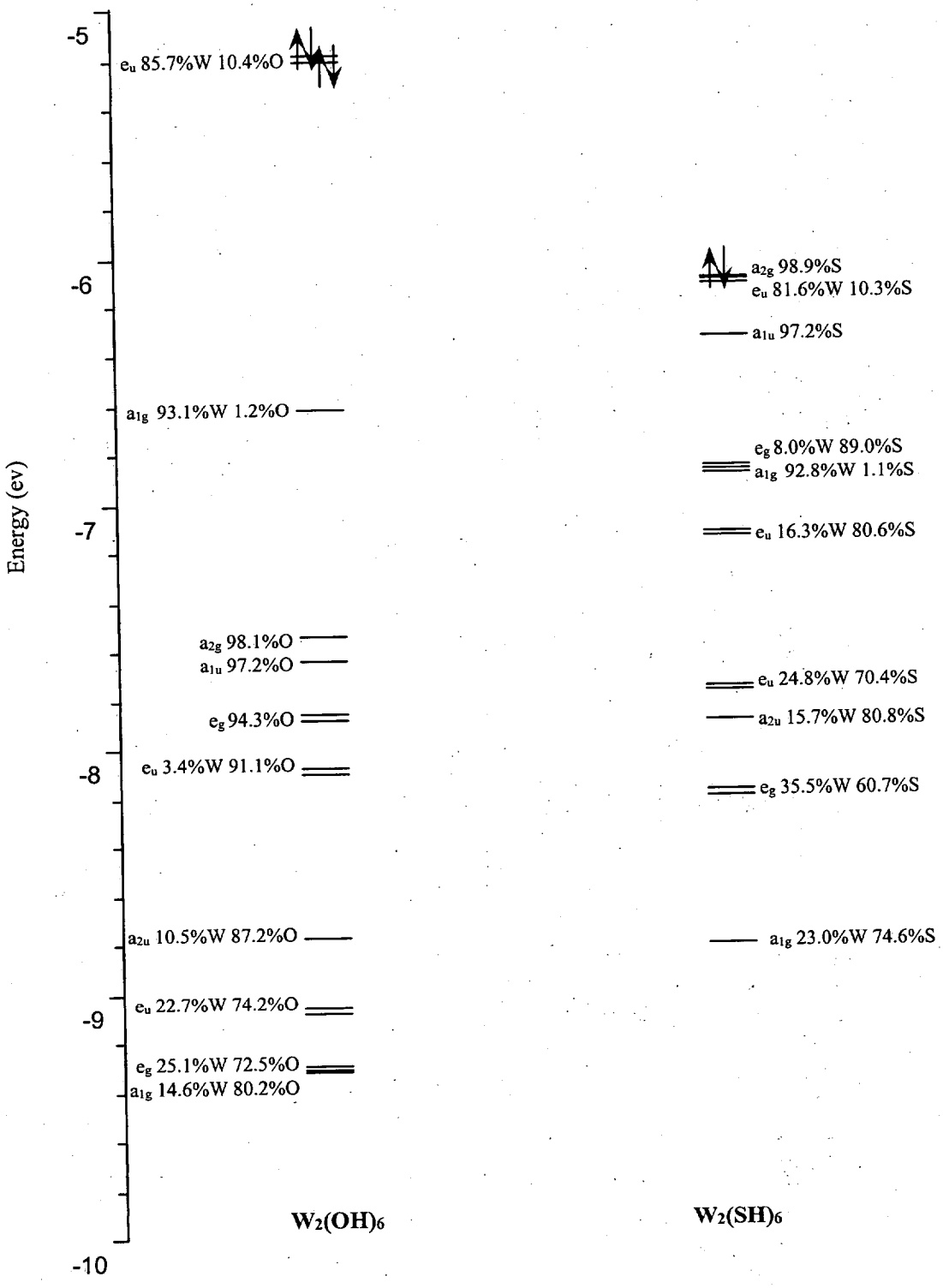
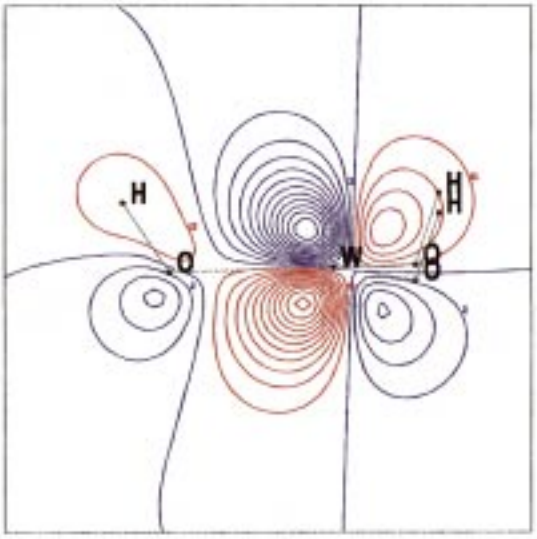
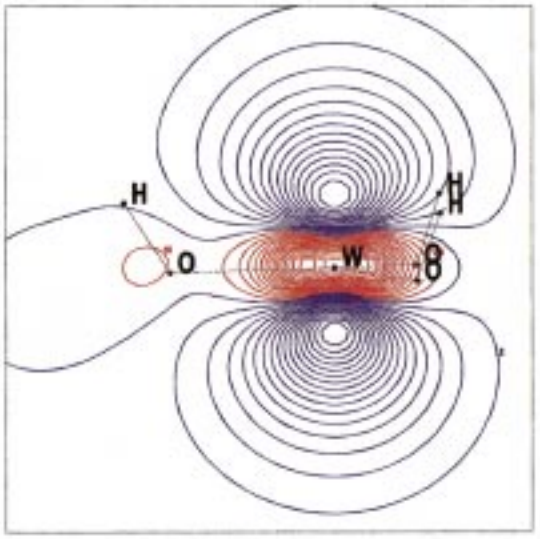


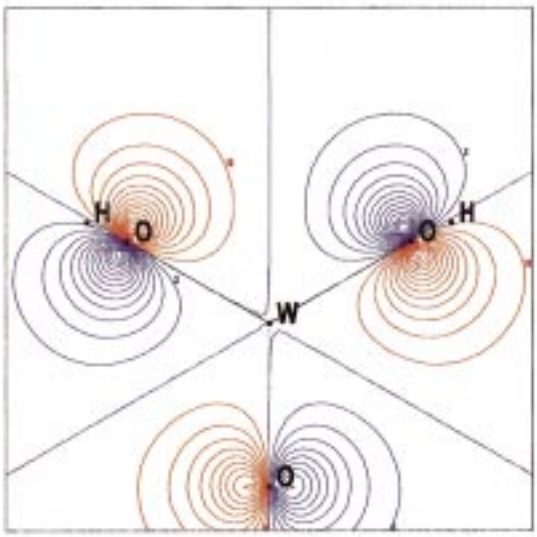
Figure 1: A comparison of the frontier molecular orbital energies for $W_2(OH)_6$ and $W_2(SH)_6$ from ADF BLYP calculations



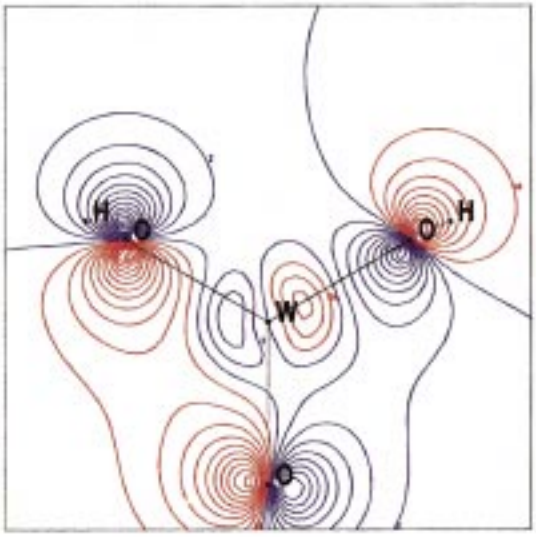
e, -5.53 eV



a_1, -6.48 eV

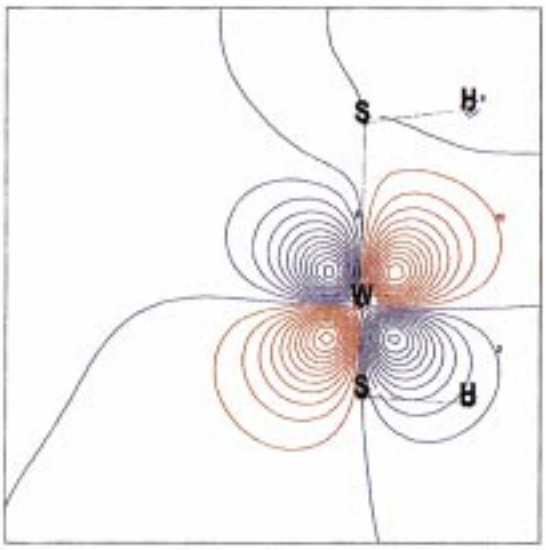


a_2, -8.65 eV

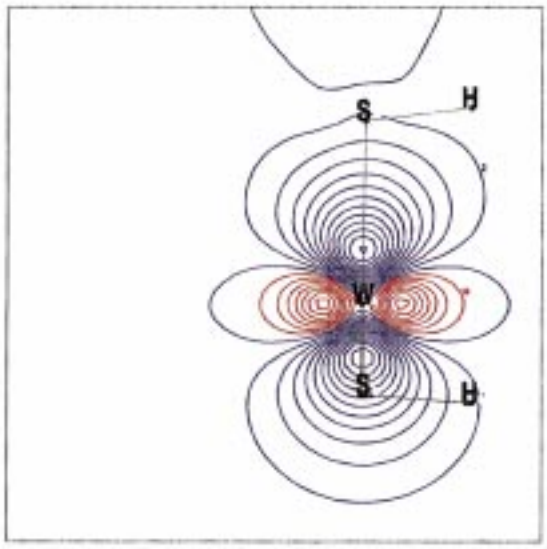


e, -9.20 eV

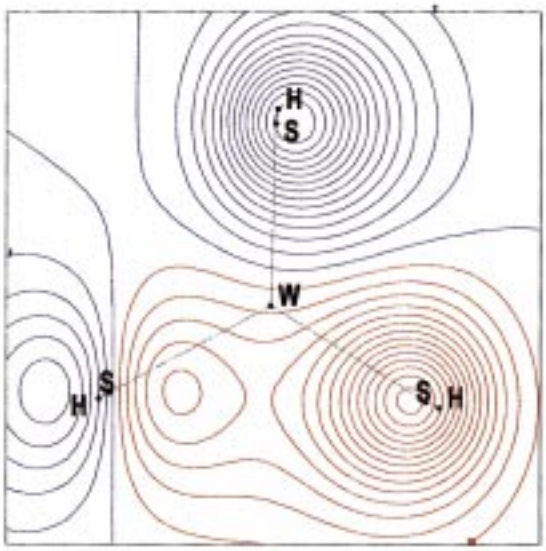
Figure 2: Frontier Molecular Orbitals for $W(OH)_3$



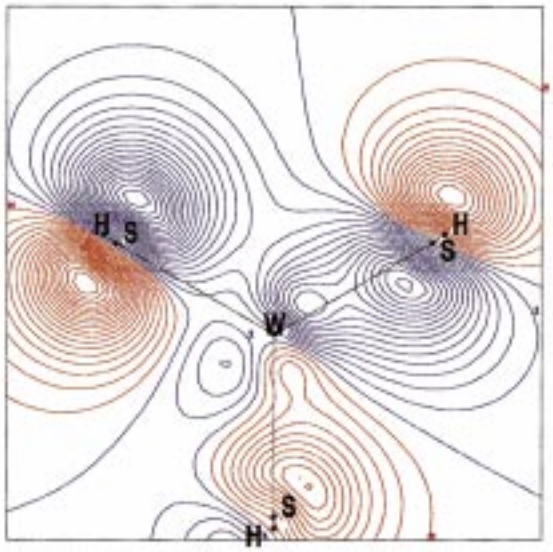
e, -6.66 eV



a_1, -6.97 eV

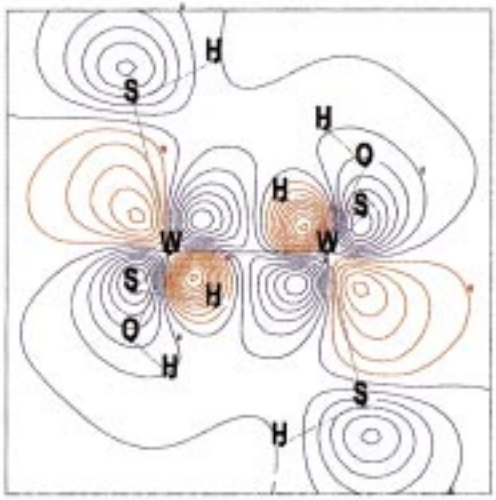


a_2, -7.07 eV

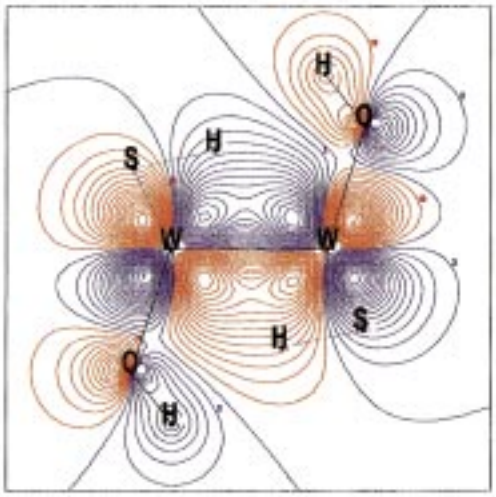


e, -7.95 eV

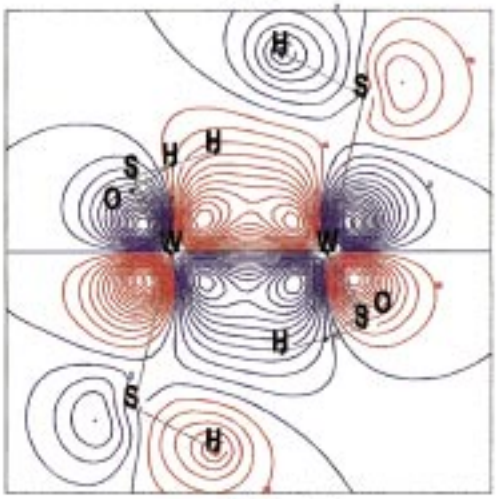
Figure 3: Frontier Molecular Orbitals for $W(SH)_3$



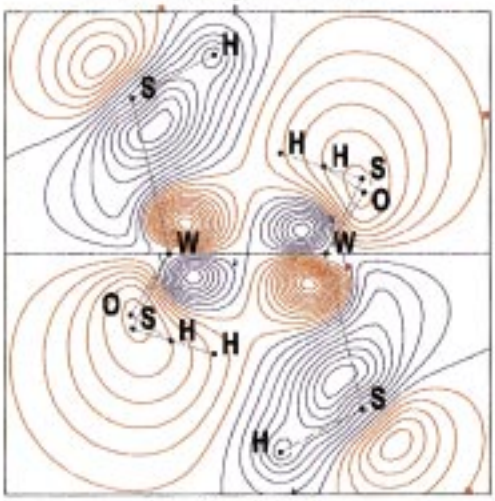
LUMO, a_g, -2.76 eV



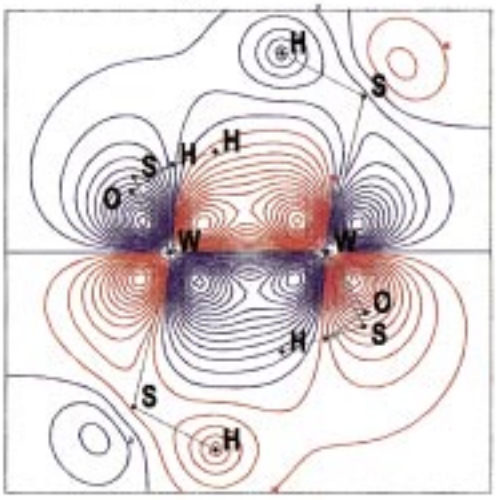
HOMO, b_u, -6.92 eV



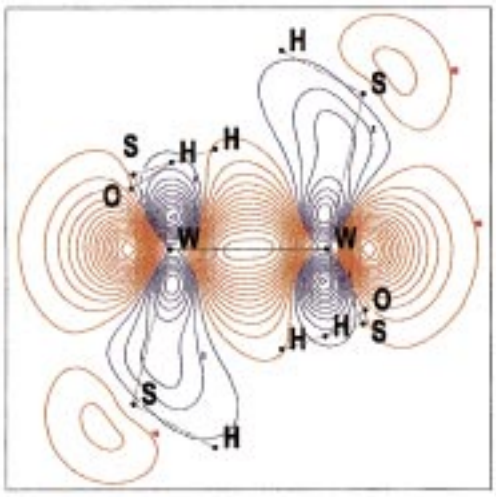
a_u, -7.26 eV



b_g, -7.34 eV

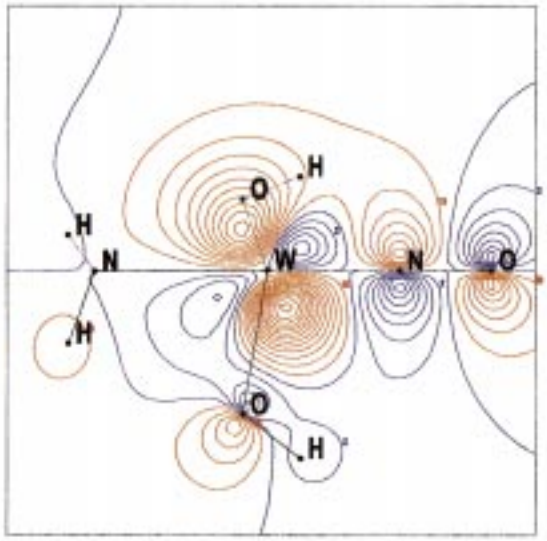


a_u, -7.58 eV

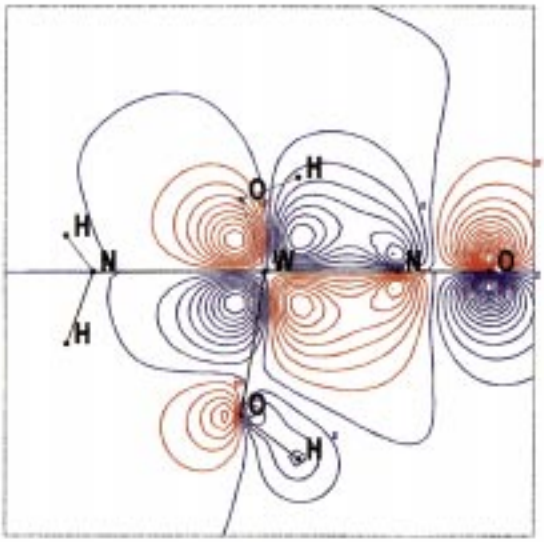


a_g, -7.91 eV

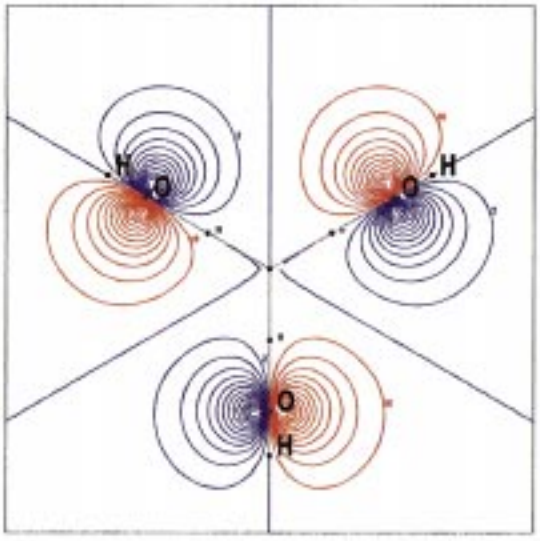
Figure 4: Frontier Molecular Orbitals for $W_2(OH)_2(SH)_4$



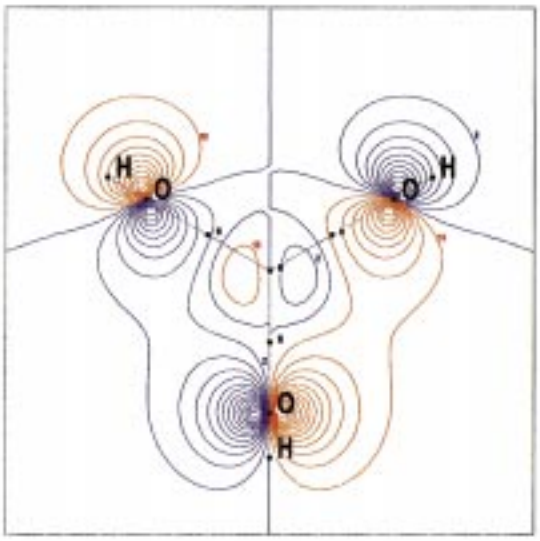
LUMO, e, -0.83 eV



HOMO, e, -5.84 eV

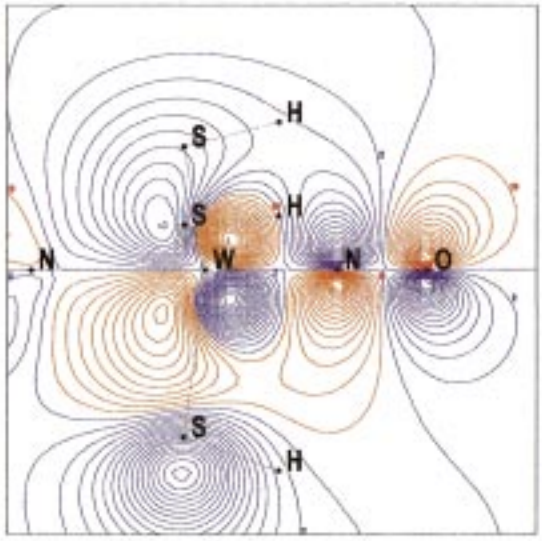


a_2, -8.58 eV

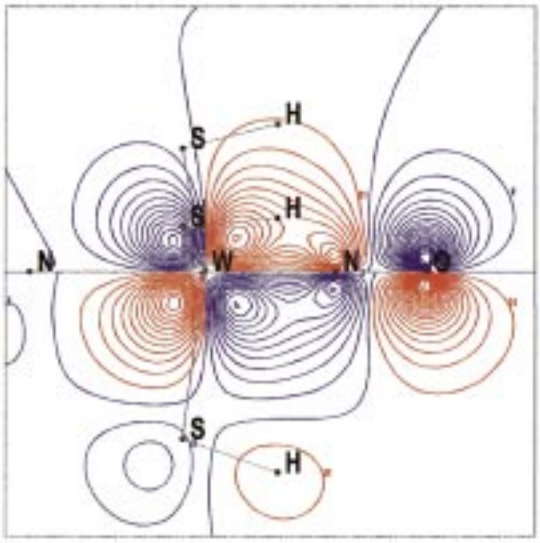


e, -8.96 eV

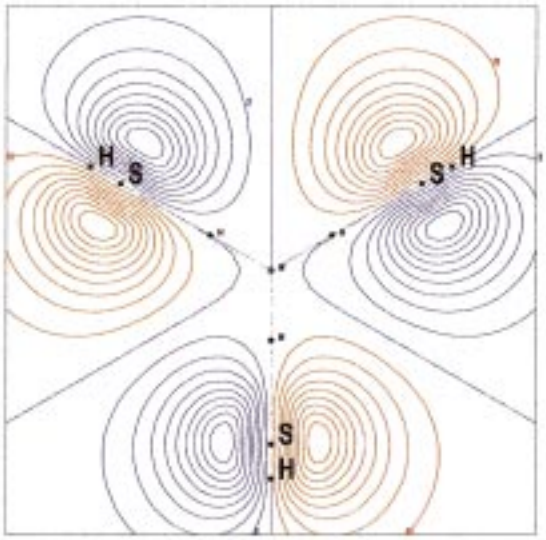
Figure 5: Frontier Molecular Orbitals for $W(OH)_3(NO)(NH_3)$



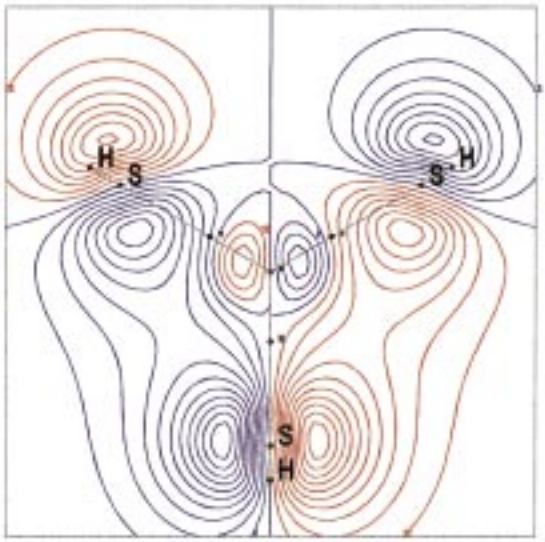
LUMO, e, -2.09 eV



HOMO, e, -6.49 eV



a_2, -6.90 eV



e, -7.67 eV

Figure 6: Frontier Molecular Orbitals for $W(SH)_3(NO)(NH_3)$