Prediction of the Bond Lengths, Vibrational Frequencies, and Bond Dissociation Energy of Octahedral Seaborgium Hexacarbonyl, Sg(CO)6

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The recent syntheses of several new elements (including the recent reports of elements 116 and 118[1]), coupled with the controversy surrounding the naming of elements 104−109, have stimulated a great interest in the chemistry of the transactinide elements.[2] We have recently been using correlated relativistic electronic structure methods in conjunction with relativistic effective core potentials (RECPs) to examine the chemistry of many hypothetical compounds of the main-group transactinide elements, such as [117]H and [118]F$_4$.[3] In this contribution, we will address the hypothetical hexacarbonyl complex of seaborgium (Sg, element 106), which is predicted to be a 6d-block transition element with six valence electrons, analogous to Cr, Mo, and W. We have previously predicted that, if it were to exist, Sg(CO)$_6$ would exhibit metal−carbonyl bonding that is very similar to that in Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$, and quite unlike that of the unknown valence isoelectronic actinide complex U(CO)$_6$.[4] This finding is in accord with the scant experimental data available for Sg.[5]

The relativistic DV-Xα method that we used in our earlier paper facilitated the analysis of the molecular orbitals of Sg(CO)$_6$, but did not allow for the calculation of total-energy properties, such as bond lengths and vibrational frequencies. Here we will use the superior methodology we have applied to other transactinide molecules to compare the bond lengths, vibrational frequencies, and CO dissociation energy of hypothetical Sg(CO)$_6$ to those of Mo(CO)$_6$ and W(CO)$_6$.[6,7]

Table 1 presents the geometries of octahedral (O_h) M(CO)$_6$ and square-pyramidal (C_{4v}) M(CO)$_5$ (M = Mo, W, Sg) molecules at the single-configuration Hartree−Fock (HF), at the correlated second-order Møller−Plesset (MP2),[8] and at the correlated coupled-cluster doubles (CCD)[9] levels of calculation. The results we obtain for Mo(CO)$_6$ and W(CO)$_6$ are similar to those obtained

Table 1. Calculated and Experimental Geometries (Å, deg) of O_h M(CO)$_6$ and C_{4v} M(CO)$_5$ Molecules

	HF	MP2	CCD	expt[a]
Mo(CO)$_6$				
Mo−C	2.126	2.045	2.076	2.063
C−O	1.118	1.161	1.147	1.145
Mo(CO)$_5$				
Mo−C$_{ax}$	2.022	1.919	1.963	
Mo−C$_{eq}$	2.126	2.043	2.075	
C−O$_{ax}$	1.126	1.175	1.158	
C−O$_{eq}$	1.118	1.162	1.148	
∠C$_{ax}$−Mo−C$_{eq}$	90.5	87.7	89.8	
∠Mo−C$_{eq}$−O$_{eq}$	179.2	177.5	177.9	
W(CO)$_6$				
W−C	2.094	2.039	2.065	2.058
C−O	1.119	1.162	1.148	1.148
W(CO)$_5$				
W−C$_{ax}$	1.989	1.927	1.950	
W−C$_{eq}$	2.096	2.034	2.061	
C−O$_{ax}$	1.130	1.175	1.161	
C−O$_{eq}$	1.119	1.164	1.149	
∠C$_{ax}$−W−C$_{eq}$	90.8	88.9	90.0	
∠W−C$_{eq}$−O$_{eq}$	179.4	178.4	178.2	
Sg(CO)$_6$				
Sg−C	2.139	2.088	2.112	
C−O	1.120	1.164	1.150	
Sg(CO)$_5$				
Sg−C$_{ax}$	2.011	1.969	1.987	
Sg−C$_{eq}$	2.133	2.078	2.105	
C−O$_{ax}$	1.133	1.177	1.164	
C−O$_{eq}$	1.121	1.166	1.152	
∠C$_{ax}$−Sg−C$_{eq}$	91.0	91.4	90.9	
∠Sg−C$_{eq}$−O$_{eq}$	179.4	179.8	179.2	

[a] Reference 13.

in recent density functional theory investigations of their electronic structures,[10,11] including a very recent study of W(CO)$_6$ that employed the zeroth order regular approximation (ZORA) to the Dirac equation.[12] For these molecules, the MP2 and CCD methods give calculated M−C bond lengths that bracket the experimental values, with the CCD results slightly better than the MP2 results. These calculations reproduce the near equality of the Mo−C and W−C bond lengths, both of which have experimental values of ∼2.06 Å.[13] The calculated MP2 and CCD Sg−C bond lengths in Sg(CO)$_6$ are 2.088 and 2.112 Å, respectively. These calculated values suggest that the Sg−C bond length in Sg(CO)$_6$ will be slightly longer than those in Mo(CO)$_6$ and W(CO)$_6$; we estimate that the experimental value would be 2.10 Å, suggesting that the atomic radius of Sg is ∼0.04 Å greater than that of Mo and W. This value compares favorably to that found in an incisive early

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(6) Computational details: shape-consistent RECPs were used to replace the inner 28, 60, and 92 electrons of Mo, W, and Sg, respectively, leaving in each case 14 metal-based electrons to be explicitly treated in the valence set.[7a−c] The valence basis sets for Mo and W were taken from the references that reported the RECPs for those atoms, whereas the basis set for Sg was optimized independently.[7d−g] In each case a (5s5p4d)/[4s4p3d] contraction scheme was used. The C and O 1s electrons were replaced by the 2e RECPs of Ermler et al.[7h] The C and O basis sets that correspond to these RECPs are from Pitzer et al. and were used with a (4s4p1d)/[2s2p1d] contraction scheme.[7i] The geometries of the M(CO)$_6$ and M(CO)$_5$ complexes were optimized under the constraints of octahedral (O_h) and square pyramidal (C_{4v}) geometries, respectively. Total energies at the CCSD(T) level were calculated at the optimized MP2 and CCD geometries. Vibrational frequencies were calculated at the MP2 level of theory only.

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study of octahedral MH_6 (M = Mo, W, Sg) by Pyykkö and Desclaux, who found that the Sg−H bonds were 0.06 Å longer than the Mo−H and W−H bonds.[14] The smaller difference in the M−CO bond lengths relative to the M−H bond lengths is a consequence of the large Sg−CO back-bonding that is discussed below.

The experimental C−O bond lengths in $Mo(CO)_6$ and $W(CO)_6$ are very well reproduced at the CCD level. The CCD value for the C−O bond length in $Sg(CO)_6$, 1.150 Å, is slightly longer than those in $Mo(CO)_6$ and $W(CO)_6$, suggesting that the M−CO back-bonding in $Sg(CO)_6$ is greater than that in $Mo(CO)_6$ and $W(CO)_6$. We will see that the calculated vibrational frequencies of $Sg(CO)_6$ are consistent with this conclusion.

The calculated geometries of the $M(CO)_5$ (M = Mo, W, Sg) are very similar. Each shows a square-pyramidal geometry with a C_{ax}−M−C_{eq} angle close to 90°. The M−C_{ax} bond length shortens considerably relative that of $M(CO)_6$, consistent with the expected greater back-bonding to the axial CO ligand in the absence of a competing *trans* ligand. As in the $M(CO)_6$ calculations, the Sg−C_{ax} is slightly longer than the Mo−C_{ax} and W−C_{ax} bond lengths. The M−C_{eq} bond lengths are nearly the same as those in the $M(CO)_6$ molecules.

The calculated MP2 CO-stretching frequencies for the $M(CO)_6$ molecules are compared to the available experimental data[15] in Table 2. With our choice of basis set, the MP2 method underestimates the frequency of free CO by 25.5 cm^{-1} (calcd, 2117.5 cm^{-1}; expt, 2143.0 cm^{-1}). Therefore, Table 2 also presents $\Delta\nu$, which is the red-shift in the frequencies of the $M(CO)_6$ molecules relative to the calculated or experimental values of free CO. The frequencies, and particularly the $\Delta\nu$ values, for $Mo(CO)_6$ and $W(CO)_6$ are satisfactorily reproduced at this level of theory. The frequencies for $W(CO)_6$ are slightly lower than those of $Mo(CO)_6$, which has been attributed in part to relativistic expansion and destabilization of the 5d shell of the former.[11] This trend is even more accentuated in the calculated frequencies for $Sg(CO)_6$, which are predicted to occur 10−25 cm^{-1} lower in energy than the corresponding vibrations of $W(CO)_6$. We attribute this red-shift, and the implicit increased Sg 6d → CO 2π back-bonding, to the greater relativistic destabilization of the Sg 6d orbitals relative to the W 5d orbitals. The lower CO stretching frequencies are consistent with the longer C−O bond lengths for $Sg(CO)_6$ noted in Table 1.

The calculated geometries and vibrational frequencies both suggest greater metal−carbonyl back-bonding in $Sg(CO)_6$ than in $Mo(CO)_6$ or $W(CO)_6$. Inasmuch as a major portion of the metal−carbonyl bond strength is attributed to back-bonding, we might expect the Sg−CO bond to be stronger than the Mo−CO and W−CO bonds. We have calculated the first carbonyl dissociation energy (FCDE) as the total energy difference between $M(CO)_6$ and $M(CO)_5$ plus free CO, corresponding to eq 1 with each species in its optimized geometry:

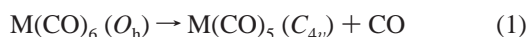$$M(CO)_6 \ (O_h) \rightarrow M(CO)_5 \ (C_{4v}) + CO \qquad (1)$$

Table 3 presents the FCDEs of the $M(CO)_6$ molecules calculated at various levels of theory, including the higher-level CCSD and CCSD(T) coupled-cluster methods.[9] The FCDEs calculated in this way correspond to the value of ΔE for eq 1. In contrast, the experimental data correspond to ΔH^{298}, which includes zero-point and thermal contributions. We have used density functional theory (DFT) calculations at the B3LYP level to estimate these additional contributions to the FCDE, and find that the values of ΔE should be reduced by ∼1.5 kcal/mol because of zero-point and thermal effects. This value is close to the 2 kcal/mol correction term calculated by Frenking et al.[10b] for $W(CO)_6$. If we assume this 1.5−2 kcal/mol correction to be largely independent of the method used to calculate it, we see that the agreement between the calculated FCDE values for $Mo(CO)_6$ and $W(CO)_6$ at the CCSD and CCSD(T) levels are well within the experimental error.[16]

Table 2. Calculated (MP2) and Experimental CO Stretching Frequencies (cm^{-1}) of $M(CO)_6$ (M = Cr, Mo, W) Molecules

mode	$Mo(CO)_6$		$W(CO)_6$		$Sg(CO)_6$
	calc	expt[a]	calc	expt[a]	calc
T_{1u}	1968.9	2003.0	1969.9	1997.6	1956.1
E_g	2002.7	2024.8	1993.3	2021.1	1967.8
A_{1g}	2093.4	2120.7	2093.7	2126.2	2085.2
$\Delta\nu^b$					
T_{1u}	−148.6	−140.0	−147.6	−145.4	−161.4
E_g	−114.8	−118.2	−124.2	−121.9	−149.7
A_{1g}	−24.1	−22.3	−23.8	−16.8	−32.3

[a] Reference 15. [b] $\Delta\nu$ is the shift of the calculated or experimental value from the calculated or experimental value for free CO.

Table 3. First Carbonyl Dissociation Energies (kcal/mol) for $M(CO)_6$ Molecules, Calculated at Various Levels of Theory[a]

method	Mo	W	Sg
MP2[b]	51.2	58.3	58.9
CCSD[b]	42.7	49.4	51.3
CCSD(T)[b]	45.4	52.0	53.0
CCD[c]	35.2	41.8	43.5
CCSD[c]	40.8	47.3	48.9
CCSD(T)[c]	43.5	49.7	50.7
expt[d]	40.5 ± 2	46.0 ± 2	

[a] The experimental values are for ΔH^{298}, while the calculated results correspond to ΔE. The latter do not include thermal or zero-point corrections, which would lower the calculated value by ∼1.5−2 kcal/mol. [b] Values calculated at the MP2 optimized geometries of $M(CO)_6$, $M(CO)_5$, and CO. [c] Values calculated at the CCD optimized geometries of $M(CO)_6$, $M(CO)_5$, and CO. [d] Reference 16.

Extrapolating to $Sg(CO)_6$, the results in Table 3 indicate that the FCDE of $Sg(CO)_6$ is slightly higher than that of $W(CO)_6$; on the basis of the CCSD(T) calculated value, we estimate that the experimental value will be 47 ± 2 kcal/mol. The greater FCDE for $Sg(CO)_6$ is again consistent with greater back-bonding in $Sg(CO)_6$ than in $W(CO)_6$. Interestingly, we find that the CO 5σ → Sg 6d forward donation is somewhat *less* than the CO 5σ → W 5d donation. $Sg(CO)_6$ thus conforms to Davidson's proposal that π-back-donation is more important to metal−carbonyl bonding than is direct σ-donation.[17]

We have not considered the possible effects of spin−orbit coupling in this work, largely because closed-shell $Sg(CO)_6$ and $Sg(CO)_5$ should be immune from dramatic first-order spin−orbit effects. Indeed, preliminary results indicate that spin−orbit effects have little impact on the calculated frequencies or FCDEs.[18]

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