Oxo and Nitrido Complexes of Molybdenum, Tungsten, Rhenium, and Osmium. A Theoretical Study[1]

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Quantum mechanical ab initio calculations at the Hartree−Fock and MP2 level of theory using relativistic effective core potentials for the metal atoms are reported for neutral and negatively charged oxo and nitrido complexes of molybdenum, tungsten, rhenium, and osmium with the general formula MXL_n (L = F, Cl; $n = 3-5$). The calculated geometries and vibrational frequencies at the HF level are in good agreement with experimental data. The analysis of the electronic structure of the complexes shows that the M−O and M−N bonds are strongly covalent but the M−L bonds have mainly ionic character. The σ and π contributions to the M−O bonds are strongly polarized toward oxygen. The M−N bonds are much less polarized and should be considered as triple bonds. The metal bonding in the M−X and M−L bonds has mainly M(d) character.

Transition metal compounds with multiple metal−ligand bonds show a fascinating variety of structures and reactivities and, therefore, have become a very active field of chemical research.[2] The most important elements forming multiple bonds with transition metals are oxygen, nitrogen, and carbon. Oxo compounds such as OsO_4, $KMnO_4$, K_2CrO_4, and Na_2FeO_4 have been known since the infant days of chemical research.[3] Nitrido complexes have also been known since the first synthesis of $K[OsO_3N]$ by Fritzsche and Struve in 1847.[4] The first imido complex *t*-$BuOsO_3N$ was reported by Clifford and Kobayashi in 1956.[5] The chemistry of transition metal nitrido and imido complexes has been considerably extended in the last two decades.[2,6] The interest in these compounds arises also from the fact that the oxo and nitrido moieties in particular are important building blocks for new electronic materials. Carbene and carbyne complexes have been known since the epochal work of Fischer.[7] Several reviews have been published regarding this field of chemical research, which has shown an exponential growth in the last two decades.[2,8]

The theoretical framework within which most of the experimental results are interpreted is provided by molecular orbital theory. The pioneering work in this field is due to Hoffmann,[9] who developed qualitative models based upon EHT calculations[10] for transition metal complexes and other compounds showing fascinating analogies between organic and inorganic molecules.[11] Because of the simplicity of the qualitative molecular orbital model, it is now widely used for transition metal complexes.[12] A drawback of this method, however, is the failure to give quantitative results. Accurate predictions of geometries and energies may be obtained from ab initio quantum mechanical methods. However, calculations based upon the Hartree−Fock (HF) approximation are expensive for transition metal compounds because of the large number of electrons, and they are also considered to be unreliable.[13] Furthermore, it is believed that this type of calculation is "difficult to interpret and understand in terms of simple qualitative concepts of bonding".[14] The results of this and other[15−22] studies demonstrate that both statements are in many cases not correct.

We have systematically studied the accuracy of theoretically predicted geometries, vibrational frequencies, and energies for closed-shell transition metal complexes using effective core potentials (ECP).[15−22] The goal of these investigations is to present a theoretical level which gives geometries and energies for transition metal compounds that are sufficiently reliable for a meaningful comparison with experimental results. The results obtained so far[15−22] allow the following conclusions: (i) The $(n-1)s^2$, $(n-1)p^6$, $(n-1)d^x$ and ns^y electrons of the transition

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metal should be treated explicitely. (ii) The geometries of transition metal complexes in *high* oxidation states are predicted with good accuracy at the HF level of theory using valence-shell basis sets of double-ζ quality. (iii) The geometries of transition metal complexes in *low* oxidation states are predicted with good accuracy at the MP2 level of theory using valence-shell basis sets of double-ζ quality. (iv) Energies calculated at MP*n* are often not reliable; the predicted relative energies frequently oscillate at different orders of perturbation theory. The best method appears to be CCSD(T).[23] (v) The electronic structure of transition metal complexes can be analyzed in a chemically meaningful way using the topological analysis of the wave function developed by Bader and co-workers[24] and by the natural bond orbital (NBO) analysis developed by Weinhold and co-workers.[25]

In our previous work, we investigated the structures of alkyne and vinylidene complexes of Mo and W,[19] carbonyl complexes of Cr, Mo, and W,[22] carbonyl and cyano complexes of Ag and Au,[20] chelate complexes of Ti,[18] iminato complexes of Ta,[16] oxo and fluoro compounds of Os,[17] and the reaction mechanism of the addition of OsO_4 to olefines.[21] In this paper, we study oxo and nitrido complexes of Mo, W, Re, and Os with the general formula MXL_n (Figure 1). We report the optimized geometries and vibrational frequencies for the M(+VI) oxo complexes MOF_4 and $MOCl_4$ (M = Mo, W, Re, and Os) and the nitrido complexes MNF_3, MNF_4^-, MNF_5^{2-}, $MNCl_3$, $MNCl_4^-$, and $MNCl_5^{2-}$ (M = Mo, W), MNF_4^- and $MNCl_4^-$ (M = Re, Os), $WNCL_2F_2^-$, $OsNF_5^{2-}$, and $OsNCl_5^{2-}$. The M(+VII) compounds $ReNF_4$ and $ReNCl_4$ have also been studied. We address particularly the oxidation state and electron population of the transition metal in these compounds. The electronic structure of the molecules is analyzed using the topological analysis of the wave function[24] and the NBO method.[25]

Theoretical Details

The geometry optimizations were performed at the Hartree–Fock and MP2 (second order Møller–Plesset perturbation theory[26]) levels of theory using the quasi-relativistic ECP developed by Hay and Wadt[27] with split valence[15] basis sets [441/2111/31] for Mo and [441/2111/21] for W, Re, and Os in conjunction with the all-electron 3–21G(d) basis set for chlorine[28] and a 6–31G(d) basis set[29] for the other atoms. For the d-type polarization functions, a set of five primitives has been used. The core electrons have been kept frozen in the MP2 calculations. The restricted open-shell Hartree–Fock method (ROHF) was employed for the open-shell d(1) compounds. The ECP incorporates the mass-velocity and Darwin relativistic terms into the potential.[27] The vibrational frequencies are calculated at the HF level of theory using numerical second derivatives of the energy. The calculations have been carried out using the Convex and Fujitsu versions of Gaussian 92.[30] For the calculation of the electron density distribution $\varrho(\mathbf{r})$, the gradient vector field $\nabla\varrho(\mathbf{r})$, and its associated Laplacian $\nabla^2\varrho(\mathbf{r})$, the programs SADDLE, GRID, and GRDVEC were used.[31] The NBO analysis[25] was carried out using Gaussian 92.[30]

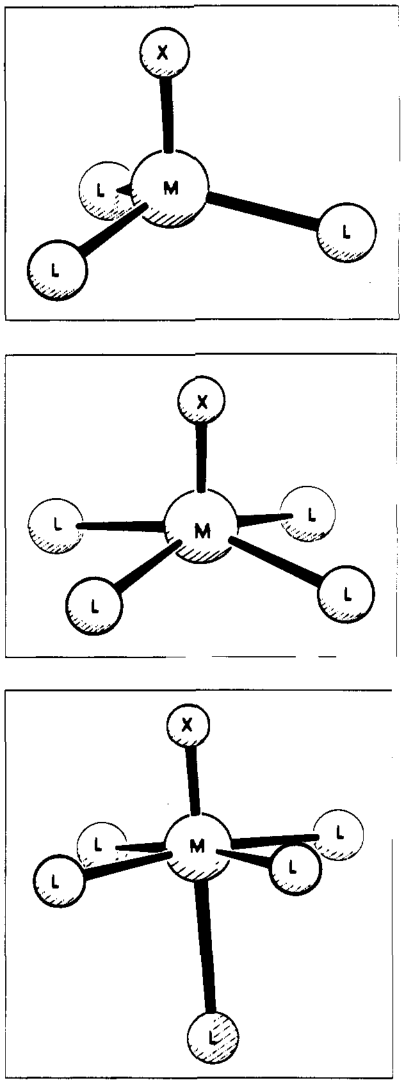

Figure 1. Structures of MXL_3, MXL_4, and MXL_5 compounds.

Results and Discussion

Table 1 shows the calculated energies and optimized geometries in comparison with experimental results. The theoretically predicted and experimentally observed vibrational frequencies are shown in Table 2.

The results for the molecular geometries shown in Table 1 demonstrate that the bond lengths and angles predicted at the HF level of theory are in satisfactory agreement with experiment. The oxo and nitrido bond lengths are in most cases calculated too short by 0.02–0.05 Å. One exception is $MoNF_4^-$, for which experimentally reported data show an unusually long Mo–N bond (1.83 Å) and a very short Mo–F bond (1.73 Å).[32] All

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Table 1. Calculated and Experimental Geometries (Bond Lengths, Å; Angles, deg) and Total Energies (hartrees)

				M−X		$M-L_{eq}$		$M-L_{ax}$		$\angle X-M-L_{eq}$		
MXL_n	sym	state	E_{tot} HF (MP2)	HF (MP2)	exp	HF (MP2)	exp	HF (MP2)	exp	HF (MP2)	exp	ref
$MoOF_4$	C_{4v}	$^1A_1$	−539.52034 (−540.81140)	1.620 (1.729)	1.650	1.835 (1.870)	1.836			105.5 (102.8)	103.8	33
$MoOCl_4$	C_{4v}	$^1A_1$	−1971.02243 (−1972.15289)	1.614 (1.755)	1.658	2.311 (2.330)	2.279			104.6 (101.4)	102.8	34
WOF_4	C_{4v}	$^1A_1$	−539.92687 (−541.13248)	1.644 (1.715)	1.666	1.834 (1.860)	1.847			105.2 (103.5)	104.8	35
$WOCl_4$	C_{4v}	$^1A_1$	−1971.39538 (−1972.43700)	1.636 (1.732)	1.684	2.311 (2.320)	2.280			104.3 (102.2)	102.6	36
$ReOF_4$	C_{4v}	$^2B_1$	−551.00532	1.614	1.609	1.834	1.823			107.8	108.8	37
$ReOCl_4$	C_{4v}	$^2B_1$	−1982.51238	1.611	1.663	2.306	2.270			106.0	105.5	37
$OsOF_4$	C_{4v}	$^1A_1$	−562.78961 (−564.03698)	1.602 (1.691)	1.624	1.840 (1.880)	1.835			110.3 (108.4)	109.3	38
$OsOCl_4$	C_{4v}	$^1A_1$	−1994.34797 (−1995.44060)	1.604 (1.720)	1.663	2.299 (2.311)	2.258			107.9 (106.1)	108.3	38
$MoNF_3$	C_{3v}	$^1A_1$	−419.65327 (−420.73135)	1.585 (1.725)		1.835 (1.858)				104.5 (103.5)		
$MoNF_4^-$	C_{4v}	$^1A_1$	−519.21066 (−520.47432)	1.596 (1.751)	1.83	1.917 (1.926)	1.73			103.7 (102.0)	99	32
$MoNF_5^{2-}$	C_{4v}	$^1A_1$	−618.52314 (−619.97358)	1.634 (1.776)		1.952 (1.956)		2.123 (2.152)		95.7 (94.2)		
$MoNCl_3$	C_{3v}	$^1A_1$	−1493.31339 (−1494.27995)	1.585 (1.722)		2.283 (2.267)				104.4 (104.5)		
$MoNCl_4^-$	C_{4v}	$^1A_1$	−1950.77232 (−1951.88307)	1.586 (1.728)	1.66	2.409 (2.386)	2.345			101.9 (101.0)	101.5	39
$MoNCl_5^{2-}$	C_{4v}	$^1A_1$	−2408.05093 (−2409.30710)	1.603 (1.737)		2.463 (2.427)		2.828 (2.766)		93.6 (92.9)		
WNF_3	C_{3v}	$^1A_1$	−419.99403 (−420.99400)	1.623 (1.718)		1.847 (1.858)				105.8 (103.3)		
WNF_4^-	C_{4v}	$^1A_1$	−519.57230 (−520.75513)	1.636 (1.732)		1.906 (1.919)				104.8 (102.5)		
WNF_5^{2-}	C_{4v}	$^1A_1$	−618.90129 (−620.26520)	1.675 (1.765)		1.938 (1.949)		2.092 (2.124)		97.2 (95.6)		
$WNCl_3$	C_{3v}	$^1A_1$	−1493.63775 (−1494.53091)	1.622 (1.718)		2.276 (2.262)				105.4 (104.2)		
$WNCl_4^-$	C_{4v}	$^1A_1$	−1951.10475 (−1952.14443)	1.624 (1.727)		2.399 (2.380)				102.9 (101.2)		
$WNCl_2F_2^-$	C_{2v}	$^1A_1$	−1235.34362 (−1236.45221)	1.632 (1.704)	2.23	2.428 (Cl) 1.884 (F) (2.392 (Cl)) (1.914 (F))	2.31 1.66			103.9 103.9 (106.1) (99.3)	81.6 129.1	46
$WNCl_5^{2-}$	C_{4v}	$^1A_1$	−2408.38849 (−2409.57275)	1.642 (1.749)		2.451 (2.421)		2.788 (2.735)		94.9 (93.6)		
$ReNF_4^-$	C_{4v}	$^2B_1$	−530.69813	1.602		1.910				106.0		
$ReNF_4$	C_{4v}	$^1A_1$	−530.52448 (−531.80106)	1.590 (1.703)		1.926 (1.851)				101.1 (102.0)		
$ReNCl_4^-$	C_{4v}	$^2B_1$	−1962.26798	1.595	1.619	2.394	2.322			103.0	103.5	40
$ReNCl_4$	C_{4v}	$^1A_1$	−1962.05259 (−1963.17426)	1.597 (1.693)	1.58	2.315 (2.309)	2.32			101.6 (101.3)	100	41
$OsNF_4^-$	C_{4v}	$^1A_1$	−542.52061 (−543.73521)	1.587 (1.699)		1.917 1.940				107.5 (106.0)		
$OsNF_5^{2-}$	C_{4v}	$^1A_1$	−641.84934 (−642.98353)	1.618 (1.776)		1.972 (1.905)		2.006 (2.149)		96.5 (94.1)		
$OsNCl_4^-$	C_{4v}	$^1A_1$	−1974.13087 (−1975.18089)	1.585 (1.693)	1.60	2.381 (2.364)	2.310			103.7 (103.6)	104.6	42
$OsNCl_5^{2-}$	C_{4v}	$^1A_1$	−2431.41614 (−2432.64371)	1.602 (1.705)	1.61	2.452 (2.423)	2.36	2.638 (2.610)	2.61	93.6 (93.0)	96.2	43

other complexes show M−N bond lengths between 1.58 and 1.66 Å. The X-ray structure analysis of $MoNF_4^-$ showed a rather large *R* value of 10.1% at room temperature (7.9% at 170 K), and strong crystal defects were noticed.[32] We note that the calculated Mo−F bond length of $MoOF_4$ at the HF level (1.835 Å) is in perfect agreement with experiment (1.836 Å)[33] and that the calculated Mo−N bond length of $MoNCl_4^-$ at the HF level (1.586 Å) is only 0.08 Å shorter than the experimental value (1.66 Å)[39]. Since the theoretically predicted and experimentally reported geometries are otherwise in good agreement, we have some doubt about the accuracy of the experimentally reported geometry of $MoNF_4^-$.[32]

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Table 2. Calculated and Experimental Vibrational Frequencies (cm^{-1}) and Calculated IR Intensities ($km\ mol^{-1}$) in Parentheses

	$\mathrm{MoOF_4}$		$\mathrm{MoOCl_4}$		$\mathrm{WOF_4}$		$\mathrm{WOCl_4}$	
	calc	exp^a	calc	exp^b	calc	exp^b	calc	exp^b
A_1	1234 (229)	1049	1207 (178)	1017	1211 (182)	1055	1196 (152)	1032
	801 (70)	714	411 (11)		807 (66)	733	408 (9)	400
	283 (21)	264	181 (5)		271 (23)	248	167 (4)	
B_2	681		291		709		302	
	105		44		115		46	
B_1	350		235		359		240	
E	808 (331)	720	409 (230)	395	782 (258)	698	384 (169)	380
	337 (13)	294	274 (1)		337 (16)	298	281 (1)	260
	254 (25)	236	146 (27)		262 (28)	236	157 (26)	

	$\mathrm{ReOF_4}$		$\mathrm{ReOCl_4}$		$\mathrm{OsOF_4}$		$\mathrm{OsOCl_4}$	
	calc	exp^c	calc	exp^d	calc	exp^e	calc	exp^f
A_1	1255 (172)	1077	1229 (143)	1040	1280 (163)	1079	1247 (146)	1032
	808 (66)	714	395 (8)	402	803 (57)		396 (6)	
	266 (18)		164 (2)		264 (14)		165 (1)	
B_2	724		310		741		337	
	109		56		106		60	
B_1	331		225		320		221	
E	789 (215)	700	382 (108)	392	800 (164)	685	402 (55)	395
	343 (20)		283 (0.2)		367 (9)	319	288 (3)	
	276 (2)		174 (5)		264 (1)		191 (0)	

	$\mathrm{MoNF_3}$	$\mathrm{MoNF_4^-}$		$\mathrm{MoNF_5^{2-}}$	$\mathrm{MoNCl_3}$
	calc	calc	exp^g	calc	calc
A_1	1303 (98)	1300 (154)	969	1208 (207)	1275 (66)
	745 (70)	679 (75)	620	621 (75)	401 (16)
	246 (20)	272 (18)		410 (119)	145 (5)
				306 (2)	
B_2		573		525	
		137		219	
B_1		296		262	
E	775 (206)	679 (292)	600	602 (316)	449 (138)
	362 (7)	368 (8)		364 (21)	296 (0)
	169 (19)	230 (25)		251 (35)	101 (22)
				130 (0)	

	$\mathrm{MoNCl_4^-}$		$\mathrm{MoNCl_5^{2-}}$	$\mathrm{WNF_3}$	$\mathrm{WNF_4^-}$
	calc	exp^h	calc	calc	calc
A_1	1278 (72)	1054	1225 (118)	1282 (92)	1269 (150)
	347 (12)	355	314 (10)	762 (72)	694 (78)
	166 (6)		155 (55)	238 (16)	264 (19)
			177 (11)		
B_2	272		242		603
	69		106		151
B_1	197		160		314
E	354 (195)	344	296 (245)	761 (156)	664 (232)
	292 (6)	278	304 (2)	354 (11)	363 (17)
	146 (18)		142 (4)	169 (18)	239 (29)
			88 (0)		

	$\mathrm{WNF_5^{2-}}$	$\mathrm{WNCl_3}$	$\mathrm{WNCl_4^-}$		$\mathrm{WNCl_5^{2-}}$
	calc	calc	calc	exp^h	calc
A_1	1195 (208)	1261 (66)	1260 (79(	1036	1221 (123)
	639 (77)	403 (14)	351 (11)	336	317 (8)
	426 (119)	135 (3)	155 (6)		162 (51)
	308 (14)				172 (5)
B_2	556		272		253
	235		69		115
B_1	277		197		166
E	596 (254)	418 (99)	331 (152)	303	276 (192)
	373 (26)	290 (1)	292 (6)	233	309 (2)
	264 (53)	103 (2)	146 (18)		145 (11)
	150 (0)				95 (1)

	$\mathrm{ReNF_4}$	$\mathrm{ReNF_4^-}$	$\mathrm{ReNCl_4}$	$\mathrm{ReNCl_4^-}$	
	calc	calc	calc	calc	exp^i
A_1	1354 (28)	1331 (115)	1306 (7)	1315 (46)	1085
	795 (52)	690 (75)	396 (5)	344 (8)	358
	286 (15)	251 (19)	171 (2)	150 (6)	
B_2	687	614	279	286	
	165	136	75	69	
B_1	344	281	228	182	
E	766 (242)	666 (210)	363 (145)	336 (118)	341
	387 (4)	354 (17)	306 (4)	291 (5)	
	238 (32)	262 (8)	123 (35)	155 (4)	

Table 2 (Continued)

	$OsNF_4^-$	$OsNF_5^{2-}$	$OsNCl_4^-$		$OsNCl_5^{2-}$	
	calc	calc	calc	exp[j]	calc	exp[j]
A_1	1375 (92)	1300 (122)	1345 (30)	1123	1306 (65)	1084
	686 (71)	612 (80)	348 (7)	358	200 (48)	384
	239 (18)	482 (99)	147 (5)	184	312 (7)	324
		278 (19)			159 (16)	184
B_2	626	561	309	352	285	334
	118	216	66	149	113	169
B_1	263	201	178	174	146	181
E	674 (184)	574 (219)	354 (89)	365	309 (57)	336
	353 (10)	345 (19)	290 (5)	271	281 (78)	264
	261 (1)	283 (14)	165 (1)	132	155 (0)	172
		194 (5)			117 (1)	146

	$WNCl_2F_2^-$ calc
A_1	1243 (102)
	675 (27)
	302 (6)
	229 (10)
	91 (2)
A_2	252
B_2	319 (153)
	282 (1)
	214 (52)
B_1	692 (222)
	375 (7)
	150 (11)

[a] Reference 50. [b] Reference 51. [c] Reference 52. [d] Reference 53. [e] Reference 54. [f] Reference 55. [g] Reference 32. [h] Reference 56. [i] Reference 57. [j] Reference 58.

The theoretically predicted M−X lengths of the oxo and nitrido bonds are significantly longer at MP2 than at the Hartree−Fock level (Table 1). It is generally known that the bond lengths of multiple bonds are calculated longer at MP2 than at HF.[44] In the present case, the HF lengths of the M−X bonds appear to be in better agreement with experiment than the interatomic distances predicted at MP2. But we want to point out that the experimental values for the M−X bonds obtained from X-ray structure analysis may be too short, because of the large difference between the atomic number of the metal atoms M and oxygen and nitrogen, respectively. This may lead to a systematic error for the experimentally reported M−X bonds. The M−L bond lengths calculated at MP2 and HF differ much less from each other than the M−X bond lengths (Table 1). The agreement between theory and experiment for the M−L bond lengths and the bond angles is quite good. We think that the deviation of the theoretically predicted M−L interatomic distances from the experimental values has the same order of magnitude as the accuracy of the experimental results. The experimentally reported value for the M−F bond length in $MoNF_4^-$ (1.73 Å[32]) is probably erroneous.

All experimentally reported mononucleic complexes MNL_4 have a tetragonal pyramidal structure, with two exceptions.[6b] One exception[45] is $TcNCl_2(PPh_3)_2$, whose structure may be affected by steric interactions. The second exception is $WNCl_2F_2^-$, which is reported to have a trigonal bipyramidal geometry.[46] Because of the reported anomaly, we included $WNCl_2F_2^-$ in our study. Table 1 shows that theory predicts a "normal" geometry for $WNCl_2F_2^-$, i.e. a tetragonal pyramid with a W−N bond length of 1.632 Å (1.704 Å at MP2). A trigonal bipyramidal structure of $WNCl_2F_2^-$ is not a minimum on the potential energy hypersurface. The X-ray analysis of the complex shows a structure for $WNCl_2F_2^-$ with two fluorine bridges that distort the tetragonal pyramidal geometry toward a trigonal bipyramid.[46] The *R* value of the X-ray structure analysis is only 9.3%.[46] We think that the experimentally reported lengths for the W−N bond (2.23 Å) and the W−F bonds (1.66 Å) are probably not correct.[46] A reexamination of the geometry of $WNCl_2F_2^-$ is suggested.

The calculated geometries for MNL_3, MNL_4^-, and MNL_5^{2-} molecules may be used to discuss the changes in the structures upon addition of L^-. MNL_3 compounds are strong Lewis acids, and they are polymeric in the solid state.[6] Therefore, experimental data are not available for isolated MNL_3 species to compare them with the calculated geometries. The calculations predict that the M−N and M−L bonds are longer in MNL_4^- than in MNL_3. A further elongation of the M−N and M−L bonds is predicted for the dianions MNL_5^{2-}. The calculations show a substantial trans effect of the M−N bond upon the M−L bond length in ML_5^{2-} (Table 1). The axial M−L bond is calculated significantly longer in the dianions than the equatorial M−L bonds. This is in agreement with the experimentally reported Os−Cl bonds in $OsNCl_5^{2-}$.[43] The lengths for the Os−Cl bonds calculated at the HF level (trans, 2.638 Å; cis, 2.452 Å) are in good agreement with the observed interatomic distances (trans, 2.61 Å; cis, 2.36 Å).[43]

The calculated vibrational frequencies shown in Table 2 may be compared with the experimental results. The theoretically predicted fundamentals are in most cases too high, particularly for the M−N and M−O stretching modes. This is known for calculated vibrational frequencies at this level of theory using the harmonic approximation.[44] The assignments of the observed frequencies to the vibrational modes agree with the theoretical vibrational spectra of the oxo and nitrido complexes (Table 2). The calculated frequencies may be useful to estimate the vibrational spectra of the complexes which have not been measured yet.

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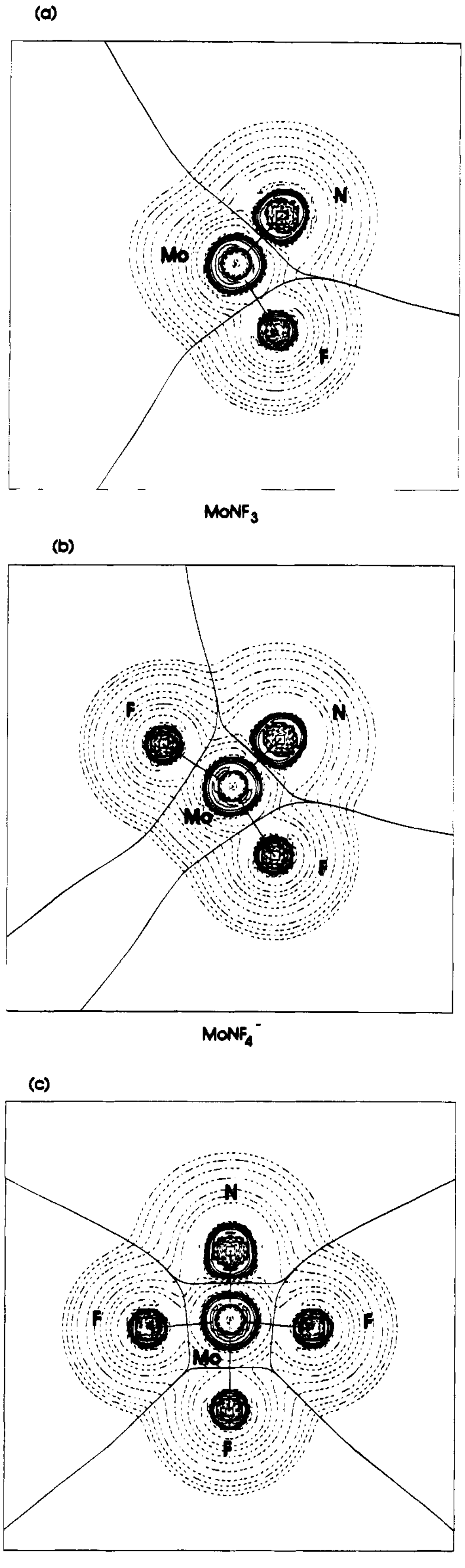

Figure 2. Contour line diagrams of the Laplacian distribution $\nabla^2\varrho(\mathbf{r})$ of (a) $MoNF_3$, (b) $MoNF_4^-$, and (c) $MoNF_5^{2-}$ in the MoNF plane. Dashed lines indicate charge depletion ($\nabla^2\varrho(\mathbf{r}) > 0$), and solid lines indicate charge concentration ($\nabla^2\varrho(\mathbf{r}) < 0$). The solid lines connecting the atomic nuclei are the bond paths, and the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the molecular plane. The crossing points of the bond paths and zero-flux surfaces are the bond critical points $\mathbf{r}_b$.

Now we turn to the discussion of the electronic structure of the nitrido and oxo complexes. We will begin with the results of the topological analysis of the wave function.[24] Figure 2 shows the contour line diagrams of the Laplacian distribution $\nabla^2\varrho(\mathbf{r})$ for $MoNF_3$, $MoNF_4^-$ and $MoNF_5^{2-}$. The shapes of the Laplacian distribution of the other molecules are very similar and, therefore, are not shown here. The results of the topological analysis are shown in Table 3.

The Laplacian distribution around the nitrogen atom shows a slightly oval-shaped distortion with an area of charge concentration ($\nabla^2\varrho(\mathbf{r}) < 0$, solid lines) directed toward the molybdenum atom. The Mo—N bond is characterized by a large negative value of the energy density at the bond critical point H_b, which indicates a strong covalent bond.[47] Typical values for covalent C—C bonds are between −2 and −3.[47,48] The covalency of the Mo—N bond decreases from $MoNF_3$ ($H_b = -2.664$) to $MoNF_4^-$ ($H_b = -2.451$) and $MoNF_5^{2-}$ ($H_b = -2.033$). The same trend is found for the other M—X bonds (Table 3). The M—O bonds of the oxo compounds are less covalent than the respective M—N bonds in the isoelectronic nitrido compounds, but they still have large negative values of H_b between −1.695 and −2.052 (Table 3).[48] The M—F and M—Cl bonds are largely ionic with only small covalent contributions to the bonding, as revealed by the low H_b values. In particular, the axial M—F and M—Cl bonds in MXL_5^{2-} are purely ionic (Table 3).

More detailed information in terms of orbital population is given by the NBO analysis.[25] Before discussing the results, we want to give a short outline about the principles of the NBO method. The one- and two-center blocks of the first-order reduced density matrix are diagonalized in such a way that natural bond orbitals are obtained which are said to represent the "best" Lewis structure of the molecule. The set of NBOs results from a transformation of the wave function into a form where a maximum number of electrons fits into a Lewis type structure. Delocalization effects appear as (weakly) occupied antibonding or Rydberg type orbitals. Since the Lewis structure does not necessarily have the same symmetry as the point group given by the positions of the atomic nuclei, the NBOs may have different symmetry. In the present case, it was found that the metal—halogen bonds are sometimes represented by the NBO analysis as strongly polarized M—L bonds, whereas in other cases no covalent bond was found. In three cases ($MoOCl_4$, $ReNF_4$, and $ReNCl_4$) the NBO gave a strong mixing of the σ and π M—X bonds, which makes the discussion of the structure in the framework of σ/π orbitals difficult. Therefore, we do not discuss the results of the NBO analysis for $MoOCl_4$, $ReNF_4$, and $ReNCl_4$.

Table 4 exhibits the calculated results for the oxo and nitrido compounds MXL_n. The NBO population analysis suggests that the M—O and M—N bonds of all investigated compounds consist of bonding contributions by one σ and two π bonds. The M—O bonds of the oxo complexes are strongly polarized toward oxygen; the metal contributions to the ϱ bonds are between 22.4% ($WOCl_4$) and 30.3% ($OsOCl_4$). The M—O π bonds are even more polarized; the metal contribution is only between 15.8% (WOF_4) and 23.4% ($ReOCl_4$). This means that the σ and particularly the π contributions to the M—O bonds have the character of a donor—acceptor bond. The trend in the polarity of the M—O bonds indicates that the effective electronegativity of the metal atoms in these compounds has the order Os > Mo ≃ Re > W.

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Table 3. Results of the Topological Analysis of the Wave Function: Laplacian Concentration $\nabla^2\varrho_b$ (e Å^{-5}), Energy Density H_b (hartrees Å^{-3}), Electron Density ϱ_b (e Å^{-3}) at the Bond Critical Point, and r_b(F) Giving the Position of the Bond Critical Point r_b for the Bond A−B Calculated by the Ratio $r_b(F) = r(A-r_b)/r(A-B)$

	$\nabla^2\varrho_b$	H_b	ϱ_b	r_b(F)
		$MoOF_4$		
Mo−O	20.41	−1.903	2.123	0.535
Mo−F	22.05	−0.239	1.066	0.525
		$MoOCl_4$		
Mo−O	21.07	−1.936	2.150	0.531
Mo−Cl	4.94	−0.146	0.635	0.491
		WOF_4		
W−O	24.41	−1.695	1.990	0.527
W−F	22.72	−0.238	0.861	0.522
		$WOCl_4$		
W−O	25.48	−1.741	2.024	0.528
W−Cl	4.63	−0.164	0.644	0.488
		$ReOF_4$		
Re−O	23.78	−2.005	2.186	0.530
Re−F	21.97	−0.296	1.100	0.520
		$ReOCl_4$		
Re−O	25.30	−1.886	2.127	0.531
Re−Cl	4.82	−0.210	0.686	0.491
		$OsOF_4$		
Os−O	25.54	−2.052	2.203	0.532
Os−F	22.55	−0.275	1.084	0.518
		$OsOCl_4$		
Os−O	26.23	−1.998	2.226	0.532
Os−Cl	4.19	−0.205	0.679	0.493
		$MoNF_3$		
Mo−N	8.39	−2.664	2.497	0.555
Mo−F	21.04	−0.182	0.990	0.522
		$MoNF_4^-$		
Mo−N	9.80	−2.451	2.400	0.544
Mo−F	18.24	−0.085	0.838	0.523
		$MoNF_5^{2-}$		
Mo−N	16.76	−2.033	2.157	0.538
Mo−F_{eq}	16.17	−0.042	0.751	0.521
Mo−F_{ax}	11.09	−0.001	0.513	0.530
		$MoNCl_3$		
Mo−N	8.75	−2.637	2.492	0.555
Mo−Cl	6.11	−0.135	0.638	0.485
		$MoNCl_4^-$		
Mo−N	10.14	−2.557	2.465	0.555
Mo−Cl	4.63	−0.071	0.487	0.483
		$MoNCl_5^{2-}$		
Mo−N	14.16	−2.390	2.360	0.545
Mo−Cl_{eq}	4.14	−0.048	0.429	0.479
Mo−Cl_{ax}	2.32	−0.012	0.207	0.482
		WNF_3		
W−N	12.07	−2.404	2.302	0.541
W−F	21.90	−0.200	1.006	0.520
		WNF_4^-		
W−N	13.22	−2.178	2.197	0.540
W−F	18.74	−0.109	0.898	0.521
		WNF_5^{2-}		
W−N	19.48	−1.756	1.958	0.528
W−F_{eq}	16.62	−0.066	0.782	0.515
W−F_{ax}	11.67	−0.030	0.565	0.529
		$WNCl_3$		
W−N	12.83	−2.382	2.302	0.541
W−Cl	5.82	−0.165	0.661	0.483
		$WNCl_4^-$		
W−N	14.45	−2.286	2.269	0.541
W−F	4.62	−0.164	0.645	0.482
		$WNCl_2F_2^-$		
W−N	12.52	−2.278	2.241	0.540
W−Cl	4.23	−0.073	0.474	0.480
W−F	19.82	−0.141	0.918	0.521
		$WNCl_5^{2-}$		
W−N	18.23	−2.481	2.361	0.524
W−Cl_{eq}	3.90	−0.061	0.439	0.480
W−Cl_{ax}	2.32	−0.016	0.218	0.485
		$ReNF_4^-$		
Re−N	15.47	−2.621	2.480	0.548
Re−F	22.40	−0.269	1.079	0.519
		$ReNCl_4^-$		
Re−N	15.87	−2.528	2.442	0.547
Re−Cl	4.40	−0.180	0.645	0.482
		$OsNF_4^-$		
Os−N	14.12	−2.559	2.476	0.547
Os−F	19.22	−0.120	0.848	0.516
		$OsNF_5^{2-}$		
Os−N	22.99	−2.162	2.257	0.532
Os−F_{eq}	16.54	−0.057	0.713	0.511
Os−F_{ax}	14.38	−0.059	0.679	0.523
		$OsNCl_4^-$		
Os−N	15.60	−2.564	2.491	0.547
Os−Cl	4.71	−0.122	0.536	0.493
		$OsNCl_5^{2-}$		
Os−N	21.55	−2.362	2.374	0.537
Os−Cl_{eq}	4.36	−0.082	0.452	0.476
Os−Cl_{ax}	3.23	−0.036	0.303	0.479

The NBO analysis shows that the nitrogen atom is a better σ and a better π donor than oxygen. The polarity of the M−N σ and π bonds toward the nitrogen atoms is always smaller than the polarity of the M−O bonds toward oxygen. The π contributions to the M−N bond of $MoNCl_4^-$, $MoNCl_5^{2-}$, and $OsNCl_5^{2-}$ are even slightly polarized toward the metal atom (Table 4). This means that the M−N bonds in the nitrido complexes should be considered as triple bonds. It is interesting to note that the polarity of the M−X σ bond in the oxo and nitrido complexes is only slightly changed upon going from the fluorine to the respective chlorine compound, whereas the M−X π bond shows larger differences (Table 4). Also, the π contributions to the M−N bonds of the nitrido complexes are less polarized than the σ contributions, whereas the opposite is calculated for the oxo complexes (Table 4).

The NBO analysis for the MOL_4 oxo complexes always shows a Lewis structure with four M−L metal−halogen bonds. The MNL_3 nitrido complexes have Lewis structures with three metal−halogen bonds. The "optimal" Lewis structure predicted for $MoNCl_4^-$ has only two Mo−Cl bonds; i.e., the NBO analysis finds the structure $MoNCl_2^+Cl^-{}_2$ as the best mesomeric form. The other MNL_4^- molecules have Lewis structures with four M−L bonds (Table 4). The best mesomeric forms for the MNL_5^{2-} complexes have only two M−L bonds, which corresponds to a set of Lewis structures $MNL_2^+Cl^-{}_3$.

The hybridization of the M−O and M−N bonds at the metal atoms shows clearly that the d-orbital contribution dominates the metal bonding in the σ and π bonds. Between 62% and 99% of the metal contribution to the M−X bonds is due to the M(d) orbitals. Also the M−L bonds show a hybridization at the metal atoms which has mainly d character. It was recently suggested[49] that in first-row transition metal complexes high

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Table 4. Results of the NBO Analysis

	metal population[a]			bond analysis[a,b]						charges			
	ns	$(n-1)$d	np	bond	pop.[c]	%M	%ns	%np	%$(n-1)$d	q_M	q_X	$q_{L_{ax}}$	$q_{L_{eq}}$
$MoOF_4$	0.21	2.75	0.06	O	1.98 (0.10)	26.8	20.8	0.2	79.0	2.98	−0.63	−0.59	
				2×O	1.88 (0.14)	16.9	0.0	33.4	66.6				
				4×F	1.92 (0.14)	8.4	19.7	33.2	48.1				
$MoOCl_4$	0.32	3.98	0.03							1.59	−0.48	−0.28	
WOF_4	0.24	2.42	0.02	O	1.99 (0.08)	22.9	23.0	0.2	76.8	3.29	−0.78	−0.63	
				2×O	1.90 (0.12)	15.8	0.0	31.4	68.6				
				4×F	1.93 (0.12)	7.4	19.2	34.4	46.4				
$WOCl_4$	0.39	3.62	0.04	O	1.98 (0.13)	22.4	15.9	0.7	83.4	1.88	−0.63	−0.31	
				2×O	1.90 (0.20)	21.3	0.0	22.8	77.2				
				4×Cl	1.85 (0.19)	15.9	20.6	38.5	40.9				
$ReOF_4$	0.24	3.68	0.03	O	0.99 (0.06)	26.2	21.7	0.3	78.0	3.01	−0.63	−0.60	
	0.12	2.26	0.01 (α)	2×O	0.93 (0.08)	16.9	0.0	35.4	64.6				
	0.12	1.43	0.01 (β)	4×F	0.96 (0.97)	10.0	15.5	30.5	49.9				
$ReOCl_4$	0.40	4.78	0.05	O	0.99 (0.08)	27.1	14.8	0.9	84.4	1.70	−0.45	−0.31	
	0.20	2.77	0.03 (α)	2×O	0.94 (0.12)	23.4	0.0	24.6	75.4				
	0.20	2.01	0.03 (β)	4×Cl	0.91 (0.11)	19.8	20.8	37.3	41.9				
$OsOF_4$	0.26	4.81	0.02	O	1.98 (0.14)	29.0	20.3	0.3	79.5	2.87	−0.54	−0.58	
				2×O	1.84 (0.18)	17.2	0.0	38.3	61.7				
				4×F	1.91 (0.16)	12.7	19.9	28.5	51.7				
$OsOCl_4$	0.43	5.86	0.02	O	1.98 (0.19)	30.3	13.7	0.7	85.6	1.60	−0.40	−0.30	
				2×O	1.84 (0.26)	22.4	0.0	30.2	69.8				
				4×Cl	1.81 (0.21)	24.3	21.1	35.0	43.9				
$MoNF_3$	0.17	3.48	0.02	N	1.93 (0.10)	38.5	22.4	0.3	77.3	2.35	−0.46	−0.63	
				2×N	1.97 (0.08)	44.8	0.0	0.6	99.4				
				3×F	1.99 (0.12)	11.2	25.7	0.5	73.3				
$MoNF_4^-$	0.20	3.39	0.02	N	1.94 (0.10)	36.5	22.9	0.3	76.8	2.36	−0.61	−0.69	
				2×N	1.84 (0.08)	37.2	0.0	23.0	77.0				
				4×F	1.93 (0.16)	6.5	19.1	38.5	42.4				
$MoNF_5^{2-}$	0.21	3.34	0.04	N	1.96 (0.09)	28.3	24.4	0.8	74.7	2.31	−0.70	−0.70	−0.80
				2×N	1.99 (0.09)	44.8	0.7	0.4	98.9				
				$2F_{eq}$	1.99 (0.19)	9.2	35.5	1.1	63.4				
$MoNCl_3$	0.29	4.33	0.02	N	1.94 (0.12)	39.2	16.8	0.6	82.6	1.35	−0.27	−0.36	
				2×N	1.96 (0.11)	49.9	0.0	0.5	99.5				
				3×Cl	1.98 (0.20)	21.1	27.2	0.9	72.0				
$MoNCl_4^-$	0.30	4.30	0.01	N	1.96 (0.14)	38.1	10.7	0.9	88.4	1.33	−0.32	−0.50	
				2×N	1.97 (0.13)	50.2	2.1	0.3	97.6				
				2×Cl	1.96 (0.35)	19.0	40.1	1.3	58.5				
$MoNCl_5^{2-}$	0.30	4.30	0.02	N	1.94 (0.21)	33.1	16.8	0.6	82.7	1.27	−0.31	−0.54	−0.81
				2×N	1.99 (0.08)	52.1	0.8	0.2	99.0				
				$2Cl_{eq}$	1.96 (0.36)	18.6	37.7	1.2	61.2				
WNF_3	0.21	3.14	0.03	N	1.96 (0.09)	34.1	24.2	0.4	75.4	2.64	−0.70	−0.65	
				2×N	1.97 (0.08)	41.0	0.0	1.2	98.8				
				3×F	1.99 (0.11)	10.5	25.2	0.6	74.3				
WNF_4^-	0.24	3.03	0.03	N	1.97 (0.09)	32.2	24.6	0.4	75.0	2.66	−0.87	−0.69	
				2×N	1.85 (0.08)	33.4	0.0	24.8	75.2				
				4×F	1.94 (0.14)	6.2	18.8	37.9	43.4				
WNF_5^{2-}	0.24	2.97	0.05	N	1.98 (0.14)	23.8	27.1	0.9	72.0	2.65	−0.99	−0.71	−0.80
				2×N	1.99 (0.10)	39.8	0.6	1.0	98.4				
				$2F_{eq}$	1.99 (0.17)	8.8	35.0	0.8	64.2				
$WNCl_3$	0.34	4.00	0.03	N	1.97 (0.11)	33.9	18.9	0.7	80.5	1.61	−0.49	−0.37	
				2×N	1.96 (0.12)	47.1	0.0	0.8	99.3				
				3×Cl	1.99 (0.18)	20.0	26.7	0.9	72.4				
$WNCl_4^-$	0.36	3.98	0.01	N	1.97 (0.11)	31.6	16.9	0.8	82.3	1.56	−0.56	−0.50	
				2×N	1.85 (0.10)	42.4	0.0	18.3	81.7				
				4×Cl	1.87 (0.20)	12.5	20.3	38.1	41.7				
$WNCl_2F_2^-$	0.30	3.44	0.01	N	1.97 (0.10)	31.8	20.9	0.5	78.6	2.20	−0.70	−0.59 (Cl)	−0.66 (F)
				N	1.87 (0.09)	31.2	0.0	23.2	76.8				
				N	1.82 (0.08)	44.9	0.0	20.6	79.4				
				2×Cl	1.89 (0.20)	10.9	22.3	38.5	39.2				
				2×F	1.93	6.5	16.7	37.0	46.4				
$WNCl_5^{2-}$	0.37	3.97	0.02	N	1.96 (0.21)	28.5	18.6	0.6	80.8	1.5	−0.57	−0.54	−0.78
				2×N	1.99 (0.09)	48.0	0.6	0.3	99.1				
				$2Cl_{eq}$	1.98 (0.33)	18.8	37.7	1.1	61.1				
$ReNF_4$	0.26	4.09	0.03							2.60	−0.21	−0.60	
$ReNF_4^-$	0.23	4.31	0.03	O	0.97	35.6	25.1	0.4	74.5	2.39	−0.63	−0.69	
	0.12	2.59	0.02 (α)	2×O	0.90	36.7	0.0	27.7	72.3				
	0.12	1.72	0.02 (β)	4×F	0.96	7.9	18.6	36.2	45.1				
$ReNCl_4$	0.42	5.18	0.03							1.31	−0.10	−0.30	
$ReNCl_4^-$	0.38	5.17	0.04	N	0.97 (0.06)	36.5	17.2	1.1	81.7	1.37	−0.29	−0.52	
	0.19	3.01	0.02 (α)	2×N	0.91 (0.05)	46.4	0.0	20.1	79.9				
	0.19	2.16	0.02 (β)	4×Cl	0.92 (0.12)	14.8	20.2	37.8	42.0				
$OsNF_4^-$	0.25	5.42	0.01	N	1.94 (0.11)	38.0	24.8	0.3	74.9	2.26	−0.49	−0.69	
				2×N	1.77 (0.10)	38.5	0.0	30.3	69.7				
				4×F	1.92 (0.19)	9.5	18.7	34.5	46.7				

Table 4 (Continued)

	metal population[a]			bond analysis[a,b]						charges			
	ns	(*n* − 1)d	*np*	bond	pop.[c]	%M	%*ns*	%*np*	%(*n* − 1)d	q_M	q_X	$q_{L_{ax}}$	$q_{L_{eq}}$
$OsNF_5^{2-}$	0.26	5.44	0.04	N	1.95 (0.20)	29.9	28.5	0.8	70.7	2.19	−0.51	−0.73	−0.77
				2×N	1.98 (0.10)	49.8	0.9	0.5	98.6				
				$2F_{eq}$	1.98 (0.24)	12.3	33.4	1.7	64.9				
$OsNCl_4^-$	0.41	6.25	0.01	N	1.95 (0.13)	38.9	18.0	1.0	81.0	1.27	−0.17	−0.53	
				2×N	1.78 (0.11)	48.2	0.0	22.8	77.2				
				4×Cl	1.85 (0.24)	17.0	20.0	37.4	42.6				
$OsNCl_5^{2-}$	0.42	6.28	0.01	N	1.94 (0.28)	34.5	21.4	0.8	77.8	1.20	−0.13	−0.58	−0.74
				2×N	1.98 (0.09)	57.6	1.0	0.3	98.7				
				$2Cl_{eq}$	1.97 (0.39)	23.1	36.0	1.7	62.3				
MoF_6	0.23	2.44	0.00							3.23		−0.54	
$MoCl_6$	0.36	4.73	0.00							0.78		−0.13	
WF_6	0.26	2.09	0.03							3.57		−0.59	
WCl_6	0.45	4.36	0.09							1.04		−0.17	

[a] *n* = 5 for Mo; *n* = 6 for W, Re, and Os. [b] pop. represents the population of the M−X or the M−L bond; %M gives the contribution of the bond at atom M; %*ns*, %*np*, and %(*n* − 1)d give the hybridization of the bond at M. [c] The first value gives the population of the bond. The population of the corresponding anti bond is given in parentheses.

oxidation states the major bonding contribution arises from interactions between the ligands and the metal 4s orbital. The results of this work suggest that metal−ligand bonding of second- and third-row transition metals is dominated at the metal by the contribution of the d orbitals.

The calculated partial charges are much lower than the formal charges in these compounds, which are considered as M(+VI) complexes (+VII in case of $ReNF_4$ and $ReNCl_4$). The highest partial charge is calculated for tungsten in WOF_4 (+3.29), which has a formal charge of +VI. For comparison, we show the calculated partial charges in the hexafluorides and hexachlorides of tungsten and molybdenum, which have a formal charge of +VI at the metal atom. The actual partial charge is as low as +0.78 for Mo in $MoCl_6$! It follows that the concept of formal charges should not be taken as measure for the actual partial charge of the metal atom.

After this study was submitted, a related theoretical work about transition metal chalcogenides by Benson et al.[58] was published. The authors report also the geometries of some oxo compounds of transition metals at the HF level of theory. The results are very similar to our data.

Summary

The theoretically predicted equilibrium geometries and vibrational frequencies of the oxo and nitrido complexes of molybdenum, tungsten, rhenium, and osmium calculated at the Hartree−Fock level of theory are in good agreement with experimental results. The oxo and nitrido bonds are predicted as significantly longer at the MP2 level. The analysis of the electronic structures shows that the M−O and M−N bonds are mainly covalent but the metal−halogen bonds are mainly ionic. The σ and π contributions to the M−O bonds of the oxo complexes are strongly polarized toward the oxygen atom. The M−N bonds are much less polarized and should be considered as genuine triple bonds. The metal bonding in the M−X and M−L bonds has mainly M(d) character. The calculated partial charges at the metal are much lower than the formal charges +VI or +VII.

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