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AM1/d Parameters for Molybdenum

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The AM1 scheme extended to d orbitals, AM1/d, has been parametrized for molybdenum. Computational results on structures and energetics of a series of molybdenum compounds are compared with experimental data. The mean absolute error of bond lengths is 0.044 Å (83 comparisons) and that of X−Mo−Y angles is 3.3° (65 comparisons). The mean absolute error of heats of formation amounts to 6.5 kcal/mol (50 comparisons). This assessment demonstrates the good performance of AM1/d. Thus, the proposed method may be used for computing structural parameters as well as heats of formations, reaction enthalpies, and bond energies of rather large inorganic and organometallic compounds of molybdenum.

Introduction

Molybdenum is an important element in both chemistry[1] and biochemistry.[2] Inorganic and metallorganic compounds of Mo are effective catalysts for chemically and industrially essential processes.[3,4] Molybdenum is the only metal of the second and third transition series that is absolutely essential for all forms of life.[5] Thus, theoretical modeling of Mo containing systems is of great interest.[6−13] Despite a tremendous increase of computational resources, high level calculations (either conventional ab initio methods accounting for electron correlation or density functional methods based on nonlocal exchange-correlation functionals) are currently applied to transition-metal compounds of small to medium size.[14−16] Therefore, many important systems, especially of biological importance which generally have no symmetry, and even reasonable models of such systems lie far beyond these approaches. As a possible approach to quantum chemical treatment of complex systems, much less demanding semiempirical methods can be used. Such approaches are able to reveal the main features and trends of a given class of systems, comparable to high level methods, but at a significantly reduced cost.[17]

Several semiempirical methods have recently been proposed for theoretical studies on bond energies and geometries of transition-metal compounds. SINDO1 has been extended to 3d transition-metals[18] and applied to organometallics of these elements.[19] The MSINDO method, suggested recently, represents a consistent modification of SINDO1 that provides an essential improvement in accuracy.[20,21] This very promising new method has not been extended yet to transition-metals. The NDDO/MC method[22] was developed to study compounds of Co and Ni. Recently, a semiempirical approach based on the NDDO approximation has been proposed and parametrized for metallorganic compounds of Cr.[23] However, so far the performance of all these schemes has been demonstrated only for several examples. ZINDO by Zerner is widely applied to calculate spectroscopic properties of 3d- and 4d-metal complexes.[24−26] Recently, a new parametrization of the NDDO methodology has been presented for some main-group elements with good results for structures and excitation energies;[27] thus far, no parameters for transition-metal atoms are available.

Nowadays semiempirical methods based on the NDDO approximation MNDO,[28] AM1,[29] and PM3[30] are widely used for computational modeling of molecular systems of main-group elements.[31] However, these MNDO-type methods in their original formulation cannot be applied to transition-metal compounds because of the omission of d orbitals. An extension of the MNDO scheme to spd basis,[32] MNDO/d, has been extensively tested for main-group elements.[33−35] The proposed treatment of two-electron two-center integrals[32] was also implemented in the PM3 method (PM3/tm model[36]) and parameters for a number of transition-metals were obtained. PM3/tm was designed to compute only geometries of transition-metal species, and therefore no reliable data on heats of formation, reaction enthalpies, and bond energies should be expected. In fact, errors in heats of formation and metal−ligand bond energies calculated with the PM3/tm method are often several tens or even hundreds of kilocalories per mole and therefore this scheme cannot be applied to energetics of transition-metal compounds. As to structural parameters, no systematic assessment of PM3/tm results has been published yet and the performance of this method remains undefined.

AM1 has been proved generally superior to MNDO in calculating organic molecules that are widely used as ligands in metallorganic chemistry. Therefore one may expect that extension of AM1 to transition-metal compounds will allow quite reasonable results to be produced. The purpose of the present work is to outline the extension of AM1 to d orbitals, to report parameters for molybdenum, and to discuss the performance of the AM1/d model.

Method and Parametrization

The extension of the AM1 method to an spd basis, AM1/d, is very similar to that used in MNDO/d.[33] The established AM1 formalism and the corresponding parameters remain unchanged for all main-group elements. Therefore, AM1 and AM1/d results are identical for all non-transition-metal atoms. To calculate two-center two-electron integrals within an spd basis, an extended multipole−multipole interaction scheme[32] is applied. All non-zero one-center two-electron integrals are retained to ensure rotational invariance. These integrals can be expressed via 17 Slater−Condon parameters that—with the exception of F^o_{sd} and G^2_{sd}—are calculated analytically using a Slater-type function with orbital exponents ζ_s', ζ_p', and ζ_d'. In turn, these exponents, as well as parameters F^o_{sd} and G^2_{sd} and one-electron core

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TABLE 1: AM1/d Parameters of Mo

U_s (eV)	−44.488	G^2_{sd} (eV)	1.200
U_p (eV)	−20.295	ρ_{core} (au)	1.334
U_d (eV)	−55.952	α_{Mo-H} (Å^{-1})	2.240
ζ_s (au)	1.945	α_{Mo-C} (Å^{-1})	2.465
ζ_p (au)	1.477	α_{Mo-N} (Å^{-1})	2.324
ζ_d (au)	2.468	α_{Mo-O} (Å^{-1})	2.492
β_s (eV)	−9.414	α_{Mo-F} (Å^{-1})	2.485
β_p (eV)	−6.180	α_{Mo-S} (Å^{-1})	2.290
β_d (eV)	−15.489	α_{Mo-Cl} (Å^{-1})	2.500
ζ_s' (au)	1.424	α_{Mo-Br} (Å^{-1})	2.130
ζ_p' (au)	1.250	α_{Mo-I} (Å^{-1})	2.150
ζ_d' (au)	1.947	α_{Mo-Mo} (Å^{-1})	2.550
F^0_{sd} (eV)	7.705		

energies, U_s and U_d, are derived from experimental valence state energies of the atomic configurations $d^{n-2}s^2$, $d^{n-1}s^1$, and d^n for Mo, Mo^+, and Mo^{2+}. Adoption of spectroscopic values of U_p in calculations leads to unrealistically high populations of the 4p valence orbitals of the metal. Therefore, the parameter U_p was adjusted. In the first step, the nine following parameters were fitted by using reference data for Mo compounds: the core energy U_p, exponents ζ_s, ζ_p, ζ_d and parameters β_s, β_p, β_d needed to calculate resonance integrals, the parameter α used in the expression of the core−core repulsion energy, and the additive term ρ_{core} needed to evaluate core−electron and core−core Coulomb interactions.[32] It is worth noting that even for main-group elements AM1 employs typically 16 adjustable parameters in an sp basis. However, our test calculations showed that there were systematic deviations for certain types of Mo-X bonds. Inclusion of Gaussian-type functions commonly used in AM1 to refine core−core repulsion terms (employing three adjustable parameters per function) did not result in significantly improved results. To overcome this deficiency we extend the AM1 scheme by introducing two bond specific parameters α_{Mo-X} and δ_{Mo-X} in the core−core repulsion term:

$$E^{core}(Mo-X) = Z_{Mo}Z_X\,\gamma_{ss}[1 + \delta_{Mo-X}\exp(-\alpha_{Mo-X}R_{Mo-X})]$$

By adopting these parameters the accuracy of the results increases significantly without introducing Gaussian functions in the core−core repulsion term. According to our experience this modification is much more efficient in the case of Mo than the inclusion of bond specific Gaussian-type functions suggested in the AM1 parametrization for boron.[37] Note that bond-type parameters are also used in SINDO,[18] NDDO/MC,[22] and MNDO/d.[33]

The adjustable parameters were fitted by using experimental enthalpies of formation and geometries for selected molecules. Different from molecules of the first- and second-row elements, reliable experimental data on the structure and energetic of transition-metal compounds in the gas phase are rather sparse. Because of that, bond distances and angles derived from crystal structures were also used for adjusting parameters. Several parametrization runs were carried out starting from different parameter values and using different training sets. A nonlinear least-squares method was used to optimize the semiempirical parameters. The resulting parameter set was tested in extensive survey calculations in order to choose the set which yields the most balanced results. The final parameters are listed in Table 1. The parameter δ_{Mo-X} is equal to 1.5 for all elements except H, C, Cl, and Mo; δ_{Mo-C} and δ_{Mo-Cl} are 2.5; δ_{Mo-Mo} is 6.0. The parameter δ_{Mo-H} is equal to R_{Mo-H} (in Å).

Calculations for open-shell systems were carried out by using the UHF method. No constraints were applied during the geometry optimization. All stationary points were checked by a vibrational analysis. The program SIBIQ[38] was used to perform the AM1/d calculations.

Results and Discussion

Energetics. Before considering heats of formation for Mo complexes we would like to make several general comments. First, even moderate deviations in calculated metal−ligand bond energies result in considerable errors in ΔH_f of complexes ML_n with a high coordination number n of the metal, since deviations in metal−ligand bond energies of each of the n M−L bonds enter into ΔH_f. On the other hand, in chemical reactions of organometallic and inorganic compounds, usually only one or two metal−ligand bonds are involved in the chemical transformation. Therefore, one expects reaction enthalpies ΔH_r to be predicted more accurately than the values of ΔH_f. Second, while AM1 predicts ΔH_f of organic molecules with average absolute error of about 5 kcal/mol for several important ligands, deviations in ΔH_f are considerably larger; a case in point is CO where the AM1 and experimental ΔH_f are −5.7 and −26.4 kcal/mol, respectively. Even if metal−ligand bond energies are reproduced rather well, errors of the calculated ΔH_f value of a complex ML_n may accumulate due to noticeable errors in the enthalpies of formation of the various ligands L. Again, calculated reaction enthalpies are not affected by errors in ΔH_f of ligands that remain unchanged during the reaction and therefore should be more reliable.

In Table 2 we compare heats of formation ΔH_f as calculated by AM1/d for molecules containing molybdenum to experimental results. Most experimental heats of formation were adopted from the compilation published in the NIST Chemistry WEB book;[39] data from other sources were also employed.[40−43] Experimental heats of formation corresponding to atomic states of Mo as derived from tables[44] are reproduced exactly due to the choice of one-center parameters.

Knowledge of the energetics of organometallics is important for understanding many catalytic reactions, in particular, the activation of hydrocarbons by transition-metal compounds. Next we consider enthalpies of formation and bond energies of several such complexes.

The AM1/d model reproduces well experimental ΔH_f values of 13 metallocene complexes (see Table 2). The average absolute deviation found for these compounds is 7.4 kcal/mol. Enthalpies of formation of organometallics without heteroatoms are predicted more accurately by AM1/d; examples are $Mo(\eta^5\text{-}C_5H_5)_2X_2$ (with X = H, CH_3, C_2H_5) and $Mo(\eta^5\text{-}C_5H_5)_2Y$ (with Y = C_2H_4 and Ph_2C_2). AM1/d consistently overestimates the heats of formation of metallocene dihalides (Table 2).

Good agreement between calculated and experimental ΔH_f values is found for two complexes with Mo−N bonds. The complex $Mo_2[N(CH_3)_2]_6$ contains a metal−metal triple bond. Since there are no experimental data for the radical $Mo[N(CH_3)_2]_3$ the bond energy of the Mo≡Mo triple bond cannot be determined unambiguously. The ambiguity arises due to uncertainty in the values of the $Mo-NMe_2$ bond energy. In addition, there is an undefined relaxation term due to a change in the metal−ligand interaction related to the breaking of the metal−metal bond. Experimental uncertainties in the metal−ligand bond energy led to the conclusion that the energy of the Mo≡Mo bond is within the range 48−188 kcal/mol.[45] This is certainly a rather wide range and does not provide a reliable result on the thermochemical strength of the metal−metal triple bond. AM1/d reproduces fairly well the ΔH_f values of $Mo[N(CH_3)_2]_4$ and $Mo_2[N(CH_3)_2]_6$ and thus may be applied to estimate the energy of the Mo≡Mo bond. According to our

TABLE 2: Calculated and Measured Heats of Formation (kcal/mol)

molecule	exptl	AM1/d	ref
Mo (s^1d^5) ^7S	157.3	157.3	39
Mo (s^2d^4) ^5D	191.2	191.2	44
Mo^+ (d^5) ^6S	322.5	322.5	40
Mo^+ (s^1d^4) ^6D	359.2	359.2	44
Mo^{2+} (d^4) ^5D	696.5	696.5	40
$Mo(C_5H_5)_2H_2$	70.4	70.6	39
$Mo(C_5H_5)_2(CH_3)_2$	79.5	78.6	39
$Mo(C_5H_5)_2(C_2H_5)_2$	70.2	60.8	39
$Mo(C_5H_5)_2(C_2H_4)$	87.2	87.9	39
$Mo(C_5H_5)_2(PhC{=}CPh)$	159.0	159.8	39
$Mo(C_5H_5)_2Cl_2$	1.0	10.7	39
$Mo(C_5H_5)_2Br_2$	28.8	39.9	39
$Mo(C_5H_5)_2I_2$	41.3	63.8	39
$Mo(C_5H_5)_2(S{-}n\text{-}C_3H_7)_2$	18.8	5.8	39
$Mo(C_5H_5)_2(S{-}i\text{-}C_3H_7)_2$	15.9	11.6	39
$Mo(C_5H_5)_2(S{-}n\text{-}C_4H_9)_2$	−1.0	−7.4	39
$Mo(C_5H_5)_2(S{-}t\text{-}C_4H_9)_2$	5.5	11.5	39
$Mo(C_5H_5)_2(SPh)_2$	90.0	91.9	39
$Mo(C_6H_6)_2$	95.9	97.2	39
$Mo(CO)_6$	−218.8[a]	−187.6	39
$Mo[N(CH_3)_2]_4$, S = 1	31.4	28.9	39
$Mo[N(CH_3)_2]_3$, S = $^3/_2$		51.3	
$Mo_2[N(CH_3)_2]_6$	30.6	36.4	39
MoO_2	−2.0	−0.9	39
MoO_3	−82.8	−79.9	39
H_2MoO_4	−203.4	−204.7	39
Mo_2O_6	−271.0	−284.3	42
$Mo_2(acet)_4$	−430.4	−423.0	39
$Mo(acac)_3$, $S = 3/2$	−285.6	−294.7	39
$Mo(O)2(acac)_2$	−289.2	−294.7	39
$Mo_2(O{-}i\text{-}C_3H_7)_6$	−370.5	−406.8	39
$Mo_2(O{-}i\text{-}C_3H_7)_8$	−515.6	−522.0	39
$MoSF_3$	−166.0	−163.4	42
$MoSF_4$	−232.0	−232.2	42
MoF_2, $S = 2$	−38.9	−41.3	39
MoF_3, $S = ^3/_2$	−145.1	−147.0	39
MoF_4, $S = 1$	−226.5	−238.5	39
MoF_5	−296.7	−310.5	39
MoF_6	−372.3	−349.0	39
MoO_2F_2	−243.0	−219.8	42
$MoOF_4$	−300.0	−293.5	39
$MoCl_3$, $S = 3/2$	−29.0	−42.4	39
$MoCl_4$, $S = 1$	−92.0	−94.2	39
$MoCl_5$, $S = 1$	−107.0	−107.5	39
$MoCl_6$	−105.0	−100.6	39
$MoOCl_4$	−141.0	−145.1	43
MoO_2Cl_2	−151.3	−155.2	39
$MoBr_2$, $S = 2$	40.0	37.8	39
$MoBr_3$, $S = 3/2$	−2.0	−9.0	39
$MoBr_4$, $S = 1$	−40.9	−46.2	39
MoO_2Br_2	−124.5	−130.3	43
MoO_2I_2	−100.4	−105.1	43

[a] Excluded from statistics.

calculation, the ground state of $Mo[N(CH_3)_2]_3$ is a quartet and the heat of formation of this radical is 51.3 kcal/mol. From these values, the dissociation enthalpy of $Mo_2L_6 \rightarrow 2MoL_3$ is calculated to be 66.2 kcal/mol.

A comparison of the calculated and observed ΔH_f values for 10 molecules with a Mo=O bond listed in Table 2 shows satisfactory agreement; the average absolute error of this class of compounds is about 5.0 kcal/mol.

The AM1/d model predicts ΔH_f values of complexes with the several types of metal−metal bonds reasonably well, e.g., the Mo−Mo double bond of $Mo_2(O\text{-}i\text{-}C_3H_7)_8$, Mo−Mo triple bonds as in $Mo_2(O\text{-}i\text{-}C_3H_7)_6$ and $Mo_2[N(CH_3)_2]_6$, and the Mo−Mo quadruple bond of $Mo_2(O_2CCH_3)_4$ (Table 2). The corresponding formal oxidation states of the metal in these compounds are Mo(IV), Mo(III), and Mo(II).

The calculated values of ΔH_f for halogen, oxo-halogen, and sulfido-halogen compounds of Mo are in reasonable agreement with experiment. Overall, the average absolute deviation of calculated ΔH_f values is about 6.5 kcal/mol for 50 comparisons (Table 2).

Geometries.[43] In Table 3, we compare calculated and observed structural characteristics of various types of molybdenum compounds.

The structural features of the fragment $Mo(Cp)_2$ are nearly constant in many compounds of the type $Mo(\eta^5\text{-}C_5H_5)_2X_2$. The structure of the complex $Mo(\eta^5\text{-}C_5H_5)_2H_2$ was characterized by high-precision neutron diffraction. An AM1/d calculation (see Table 3) reproduces the eclipsed configuration of the two cyclopentadienyl rings found experimentally.[46] The ligand C_5H_5 exhibits a slightly deformed penthahapto coordination; Mo−C distances range from 2.286 to 2.421 Å according to an AM1/d calculation; in the crystal structure the corresponding range is from 2.238 to 2.326 Å.[46] The Mo−H distance predicted by AM1/d is 0.14 Å shorter than the measured bond length, while the H−Mo−H angle of 75° is well reproduced. Similar results are obtained for $MoCp_2Cl_2$ (see Table 3).[47]

Apart from the cyclopentadienyl anion $C_5H_5^-$ two other aromatic 6π ligands were considered, neutral C_6H_6 and the cation $C_7H_7^+$. Within Mo(IV) compounds these rings are approximately planar. The individual C−C bonds of these rings exhibit no significant variation. The AM1/d model reproduces Mo−C distances well in the π-complexes considered. The arene ligands in $[Mo(C_6H_6)_2]^+$ are parallel to each other and they adopt a staggered conformation, in accord with X-ray data obtained for $[Mo(C_6H_6)_2][FeBr_4]$.[49]

Compounds with a Mo−Mo bond. Molybdenum displays a remarkable propensity to form metal−metal bonds in all of its oxidation states.[1] There are a large number of Mo_2X_6 compounds (X = C, N, O, S) which contain Mo≡Mo triple bonds and adopt a staggered, ethane-like geometry without bridging groups. The complex $Mo_2(NMe_2)_6$ deviates slightly from D_{3d} structure. The $MoNC_2$ moieties are essentially planar; the dihedral angle CNNN (three N centers coordinating to the same Mo center) is calculated to deviate less than 3° from the ideal value of 90° characteristic of the D_{3d} structure. A calculation with a D_{3d} symmetry constraint yields heat of formation of the complex which is about 1 kcal/mol higher than that of a full geometry optimization. The AM1/d model predicts the Mo≡Mo distance to 2.222 Å, which is in good agreement with the experimental value of 2.214 Å.[54] Very good agreement between calculated and observed data is obtained for $Mo_2(MeNCH_2CH_2NMe_2)_3$, a complex of similar structure.[56] In hexabenzyldimolybdenum, $Mo_2(CH_2Ph)_6$, the calculated Mo−Mo bond distance and the bond angles Mo−Mo−C and C−Mo−C are in good agreement with X-ray data, while the Mo−C distance is by 0.05 Å shorter than the observed value (Table 3).[57] Results of similar accuracy are also found for the 1,2-dimetallacyclic compound $Mo_2(CH_2)_4(NMe_2)_4$. In this compound, which exhibits a metal−metal triple bond, all calculated structural characteristics of the six-membered ring are well reproduced, with the exception of the Mo−C distance, which is calculated too short.

Tetra-μ-acetatodimolybdenum(II), $Mo_2(O_2CCH_3)_4$, is an important example of compounds with a Mo−Mo quadruple bond. The calculated Mo−Mo distance of 2.161 Å is somewhat longer than that observed in the free molecule (2.079 Å[51]) and in the crystal structure (2.093 Å[35]). The Mo−O bond lengths and the

TABLE 3: Calculated and Measured Bond Lengths (Å) and Bond Angles (deg)

molecule	variable	exptl	AM1/d	ref
$MoCp_2H_2$	Mo—C′	2.277	2.286	46
	Mo—C″	2.326	2.338	
	Mo—H	1.685	1.547	
	H—Mo—H	75.5	79.5	
$MoCp_2Cl_2$	Mo—C	2.320	2.298	47
	Mo—Cl	2.464	2.339	
	Cl—Mo—Cl	82.0	83.0	
$Mo(C_5H_4CH_3)_2O$	Mo—C	2.370	2.399	48
	Mo═O	1.721	1.645	
	O═Mo—C′	83.8	84.3	
	O═Mo—C"	134.4	140.1	
$Mo(C_6H_6)_2+$	Mo—C	2.260	2.267	49
$Mo(C_7H_7)(CO)_3+$	Mo—C (ring)	2.314	2.162	50
	Mo—CO	2.032	2.059	
	OC—Mo—CO	85.2	80.6	
$Mo(CO)_6$	Mo—C	2.063	2.027	51
$MoCp(CO)_3Cl$	Mo—C	2.323	2.486	52
	Mo—CO	2.009	2.071	
	Mo—Cl	2.498	2.449	
	Cl—Mo—CO	77.2	76.2	
	Cl—Mo—CO′	136.7	140.4	
	CO—Mo—CO′	78.4	79.1	
$Mo[N(CH_3)_2]_4$	Mo—N	1.980	1.960	53, 54
$Mo_2[N(CH_3)_2]_6$	Mo═Mo	2.214	2.222	53, 54
	Mo—N	1.980	1.972	
$Mo(O)_2(Acac)_2$	Mo═O	1.690	1.647	58
	Mo—O_{cis}	1.980	1.959	
	Mo—O_{trans}	2.190	2.172	
	O═Mo═O	105.0	101.3	
MoF_6	Mo—F	1.820	1.853	51
MoO_2F_2	Mo═O	1.750	1.650	51
	Mo—F	1.820	1.842	
	F—Mo—F	113.0	120.1	
	O═Mo═O	109.5	102.2	
$MoOF_4$	Mo—O	1.650	1.641	51
	Mo—F	1.836	1.838	
	O—Mo—F	103.8	107.7	
	F—Mo—F	86.7	84.6	
$MoCl_4$	Mo—Cl	2.230	2.233	51
$MoCl_5$	Mo—Cl_{eq}	2.270	2.265	51
	Mo—Cl_{ax}	2.270	2.189	
$MoCl_6$	Mo—Cl	2.260	2.246	43
$MoOCl_4$	Mo—O	1.658	1.624	51
	Mo—Cl	2.279	2.260	
	O—Mo—Cl	105.0	105.2	
MoO_2Cl_2	Mo═O	1.698	1.642	51
	Mo—Cl	2.259	2.249	
	Cl—Mo—Cl	112.0	120.2	
	O═Mo═O	104.0	101.0	
$MoBr_4$	Mo—Br	2.390	2.368	51
MoO_2Br_2	Mo═O	1.700	1.642	43
	Mo—Br	2.420	2.381	
	Br—Mo—Br	110.0	118.0	
$Mo(S_2CNMe_2)_2O_2$	Mo═O	1.696	1.649	62
	Mo—S	2.446	2.486	
	O═Mo═O	105.7	103.2	
	O═Mo—S	81.6	86.2	
	S—Mo—S′	68.4	67.7	
	O═Mo—S	113.5	110.7	
	O═Mo—S′	93.5	97.5	
MoO_2Lig [a]	Mo═O	1.689	1.643	64
	Mo—S	2.420	2.370	
	Mo—N	2.410	2.426	
	O═Mo═O	109.1	99.3	
	S—Mo—S	160.6	155.5	
	N—Mo—N	74.8	77.3	
	O—Mo—N	89.1	91.2	
	S—Mo—N	78.2	79.2	
$MoO_2(SCMe_2CH_2NHMe)_2$	Mo═O1	1.723	1.672	63
	Mo═O2	1.711	1.672	
	Mo—S	2.409	2.355	
	Mo—N	2.262	2.324	
	O═Mo═O	122.2	112.4	
	S—Mo—S	69.8	87.9	
	N—Mo—N	144.0	150.0	
	O1═Mo—S1	107.6	108.8	
	O1═Mo—S2	119.5	118.8	
	N1═Mo—S1	72.9	74.6	
	N1═Mo—S2	142.0	135.3	
$Mo_2(CH_2)_4(NMe_2)_4$	Mo—Mo	2.200	2.210	55
	Mo—C	2.165	2.109	
	Mo—N	1.960	1.940	
	Mo—Mo—C	97.0	96.2	
	Mo—Mo—N	105.0	103.7	
	N—Mo—N	122.4	119.4	
$Mo_2(MeNCH_2CH_2NMe_2)_3$	Mo—Mo	2.190	2.216	56
	Mo—N	1.969	1.936	
	Mo—Mo—N	101.8	101.1	
	N—Mo—N	116.1	115.9	
	Mo—Mo—N	103.7	102.7	
$Mo_2(CH_2Ph)_6$	Mo—Mo	2.175	2.193	57
	Mo—C	2.162	2.114	
	Mo—Mo—C	97.6	96.5	
	C—Mo—C	118.3	118.2	
$Mo_2(O_2CCH_3)_4$	Mo—Mo	2.079	2.161	51
	Mo—O	2.108	2.010	
	Mo—Mo—O	92.2	91.9	
$Mo_2(O_2CCF_3)_4$	Mo—Mo	2.105	2.165	51
	Mo—O	2.102	2.016	
	Mo—Mo—O	91.9	92.0	
Mo_3O_9	Mo═O	1.670	1.652	51
	Mo—O	1.890	1.847	
	O═Mo═O	106.4	103.0	
$MoO_2F_4{}^{2-}$	Mo═O2	1.710	1.687	58
	Mo—F_{cis}	1.940	1.903	
	Mo—F_{trans}	1.970	1.957	
	O—Mo—O	95.0	100.5	
$MoOCl_4$-	Mo—O	1.670	1.627	59
	Mo—Cl	2.333	2.315	
	O—Mo—Cl	105.2	106.5	
$NMoCl_4$-	M═N	1.637	1.655	60
	Mo—Cl	2.344	2.303	
	N═Mo—Cl	103.1	101.7	
$NMoBr_4$-	M═N	1.630	1.655	60
	Mo—Br	2.488	2.442	
	N═Mo—Br	103.0	102.0	
MoO_3(dien)	Mo═O	1.736	1.674	58
	Mo—N	2.326	2.225	
	O—Mo—O	105.8	103.8	
$(MoNCl_3)_4$	Mo═N	1.660	1.667	58
	Mo—N	2.180	1.996	
	Mo—N—Mo	167.3	165.5	
	Mo—N′-Mo	178.3	169.4	
$Mo(S_2CNMe_2)_2O$	Mo═O	1.664	1.624	62
	Mo—S	2.420	2.387	
	O═Mo—S	111.7	109.5	
	S—Mo—S	72.3	72.6	
	S═Mo—S	140.1	141.3	
$MoO_2(CH_3)_2$bpy	Mo═O1	1.707	1.646	65
	Mo═O2	1.708	1.650	
	Mo—CH3	2.194	2.136	
	Mo—N	2.314	2.397	
	Mo—N	2.346	2.416	
	O═Mo═O	110.2	101.4	
	N—Mo—N	68.4	70.8	
	C—Mo—C	149.0	148.3	
	O—Mo—C	99.8	98.7	
$MoO_2(bpy)Br_2$	Mo═O	1.734	1.644	66
	Mo—Br	2.626	2.468	
	Mo—N	2.354	2.347	
	O═Mo═O	103.3	99.3	
	N—Mo—N	66.9	72.2	
	Br—Mo—Br	159.7	152.6	
	O—Mo—Br	99.8	98.9	
$MoO_2(bpy)(O_2)_2$	Mo═O	1.692	1.637	67
	Mo—O	1.953	1.940	
	Mo—N	2.199	2.186	
	N—Mo—N	70.9	72.1	
	O—Mo—O	44.4	39.3	
	O═Mo—O	105.6	105.8	

[a] Lig = $SCH_2CH_2NMeCH_2CH2_2NMeCH_2CH_2S$, a linear tetradentate ligand with two amino and two thiolate sulfur donor groups.

Mo−Mo−O bond angles are predicted close to experimental values.[51] A comparison of the structures of the complexes $Mo_2(O_2CR)_4$ with R = CH_3 and CF_3 (see Table 3) suggests the molecular geometry to be insensitive to the nature of the substituent R.

Inorganic Compounds. In Table 3 we also compare calculated and observed geometries for about 20 inorganic molecules and ions. Inspection of these data reveals that the AM1/d models provides satisfactory estimates of Mo−halogen bond distances in compounds with four-, five-, and six-coordinated Mo centers. The absolute average deviation is about 0.02 Å. Note that the available electron-diffraction data[51] are not sufficient for establishing the equilibrium configuration of the molecule $MoCl_5$ in the gas phase. The AM1/d model predicts a C_{4v} structure with distances $Mo-Cl_{ax}$ and $Mo-Cl_{eq}$ of 2.189 and 2.265 Å, respectively; the angle $Cl_{ax}-Mo-Cl_{eq}$ is calculated to 110.2°. The calculated average Mo−Cl distance, 2.25 Å, is close to the experimental value of 2.27 Å.[51]

The AM1/d model consistently underestimates Mo−O distances by about 0.05 Å (Table 3). The angle O═Mo═O of [MoO_2] fragments is usually calculated smaller than observed. While the Mo−N single bond distance is well reproduced by AM1/d, the calculated double and triple bonds lengths are slightly longer as compared with experiment. AM1/d predicts the Mo−S distances to be somewhat shorter (by about 0.05 Å) than those found in crystal structures.

The tetrameric nitrido complex $(MoNCl_3)_4$ exhibits an interesting structure. According to an AM1/d calculation, the Mo−N−Mo bridges of the complex are slightly bent (the bond angle is about of 170°). The Mo−N−Mo bridges are found to be asymmetric both in the calculation and in the crystal structure.[58] The bridges feature one short and one longer Mo−N bond and may be presented as Mo═N−Mo; calculated and observed bond lengths are in a good agreement (see Table 3).

Catalytic Site of Molybdenum Enzymes. The problem of modeling the active sites of oxygen-transfer enzymes have been widely discussed.[2,5,69] The majority of these studies focused on a structural characterization of the complexes $Mo^{(IV)}OL_n$ and $Mo^{(VI)}O_2L_n$ and their relationship to the structure of the molybdenum coordination sphere in the active site of the enzymes.

First we consider the geometry of two oxo molybdenum dithiocarbamates, $Mo^{(IV)}O(S_2CNR_2)_2$ and $Mo^{(VI)}O_2(S_2CNR_2)_2$. AM1/d calculations were carried out for complexes with R = CH_3. The mono-oxo complex adopts a square pyramidal geometry, where the basal plane is formed by the four sulfur atoms (Table 3). The Mo═O bond, perpendicular to the basal plane, is calculated to 1.624 Å, in satisfactory agreement with the observed value of 1.664 Å.[62] The four Mo−S bonds, calculated to 2.387 Å, agree well with experiment, 2.420 Å. The observed O═Mo−S bond angles are also correctly reproduced (AM1/d: 109.5°; exptl 110.3°). The dioxomolybdenum(VI) complex $MoO_2(S_2CNR_2)_2$ exhibits a deformed octahedral structure with two cis-oxygen atoms. Compared to the four-coordinated Mo complex, this six-coordinated structure features longer Mo═O distances, by 0.03 Å;[62] the AM1/d values reflect this experimentally found bond lengthening accurately (Table 3). Bond angles of this complex are accurately reproduced by AM1/d as can be seen in Table 3.

The molecule $MoO_2(SCH_2CH_2NMeCH_2CH_2NMeCH_2CH_2S)$ provides also a model system for the metal coordination in molybdenum-containing enzymes.[64] While this compound exhibits an irregular geometry in the crystal structure,[64] AM1/d predicts a symmetric structure with the C_2-axis bisecting the angles O═Mo═O and S−Mo−S (Table 3). The pairs of calculated Mo═O, Mo−N, and Mo−S distances are equivalent with bond lengths of 1.64, 2.37, and 2.43 Å, respectively, in good agreement with experiment.[64] The calculated bond angle O═Mo═O of 99.3° falls somewhat outside the range of 102−109°, usually observed for $MoO_2 2+$ species.

In summary, the AM1/d model correctly predicts molecular geometries of various Mo containing species. The mean absolute error of calculated bond lengths is about 0.044 Å (83 comparisons). Bond distances are consistently calculated too short; the mean error is −0.028 Å. The mean error and the mean absolute error of bond angles found from 65 comparisons are −0.3° and 3.3°, respectively.

Conclusions

Based on the reported results we conclude that the AM1/d model may be applied to predict semiquantitatively the energetics and the structures of molybdenum compounds. Therefore the AM1/d model allows a theoretical description of rather large and complex organometallic and bioinorganic systems. An AM1/d parametrization of Ti has been established in a similar fashion; it will be published elsewhere.[70]

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