PM3(tm) Analysis of Transition-Metal Complexes

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Transition-metal complexes with prototypical ligands were studied using the PM3(tm) semiempirical method. The calculated complexes in this paper include 35 halides, 7 aqua complexes, 7 tris(ethylenediamine) complexes, 27 multiply bonded complexes, and 19 organometallics. PM3(tm)-predicted geometries were compared with the experimental data from 1200 crystal structures. For multiply bonded complexes, a comparison was also made between PM3(tm) and higher level calculations employing effective core potentials and MP2 wave functions. In general, PM3(tm) was quite successful in predicting the geometries of transition-metal complexes, especially those incorporating metals from the left-hand side of the transition series.

INTRODUCTION

It is well-known that transition-metal (TM) complexes are very important in many areas of chemistry, such as catalysis, advanced materials, and biochemistry.[1] Treating TM complexes using quantum chemistry techniques is a major challenge because the modeling of relatively large systems is very time-consuming. Semiempirical quantum methods are much faster than ab initio methods and, thus, have great potential to provide acceptable results for studying relatively large molecules. Greater speed comes at the expense of approximations made in evaluating the integrals that describe interactions among the nuclei and electrons—some integrals (those deemed to be negligible) are ignored, while others are estimated from experiment. Hence, semiempirical results must be rigorously evaluated by comparison with experiment before they are applied to new systems. PM3 is believed to be a distinctive improvement over other semiempirical methods in the prediction of geometries.[2] Its successful applications in inorganic chemistry include the study of semiconductor oxides and their interaction with gas molecules,[3−5] descriptions of hypervalent molecules,[6,7] calculation of hydration energies of metal cations,[8] and investigation of complexes made by main-group 14 and 15 elements.[9,10] PM3 was, however, found to be inadequate for the description of hydrogen-bonded systems[11,12] and for calculating barriers to internal rotation.[13]

PM3(tm) is an extension of the standard PM3 Hamiltonian for transition-metal elements, but published applications and evaluations are rare. A literature review shows that published papers have concentrated on a few specific, chemically-related compounds. Adam and co-workers reported on the limitations of PM3(tm) in treating nickel(II) amine complexes.[14] However, Børve et al. achieved satisfactory results for Ti, Cr, and Zr organometallics.[15] Decker and co-workers obtained very good agreement between experimental and PM3(tm)-calculated results for the prediction of geometries of dinuclear manganese complexes such as $Mn_2(CO)_6(H_2-PCH_2PH_2)_2$.[16] Cundari et al. reported the successful prediction of geometries with an extension of the PM3(tm) method for vanadium.[17]

Transition-metal complexes are found with a myriad of ligand types, coordination numbers, bond types, and oxidation states. It is not feasible to select a representative assortment of *all* metals with *all* reasonable ligand types. Also, the PM3(tm) parameterization is not yet available for all 30 d-block metals. Our main intention was to survey a variety of coordination environments, coordination complexes, and organometallics to evaluate the predictive ability of the PM3(tm) technique for geometries.

COMPUTATIONAL METHODS

PM3(tm), like other semiempirical methods, is a self-consistent-field (SCF) method. All calculated integrals are evaluated by approximate means.[2] A PM3(tm) calculation can be divided into two parts: PM3 for main-group elements, which uses a valence basis set of one ns orbital and three np orbitals per atom; PM3(tm) for transition metals describes the nd, $(n + 1)$s, and $(n + 1)$p valence orbitals and the electrons contained therein. It differs from MNDO in the treatment of the core repulsion function (CRF), which is extensively parameterized in PM3. PM3(tm) uses only single-atom parameters, while MINDO/3[18] uses both single and diatomic parameters and was reparameterized using a radically different optimization procedure. The parameters for PM3 (main group) have been arrived at by fitting experimental data for equilibrium structures, heats of formation, dipole moments, and ionization potentials.[19] The parameters for PM3(tm) are based on fitting experimental structure data only.

Calculations employed the PM3(tm) Hamiltonian incorporated in the Spartan (version 5.0) program. All geometries were fully optimized, and the nature of the resulting stationary point was characterized by harmonic vibrational frequencies at the PM3(tm) level. Bond lengths were compared with experimental data and, in the case of multiply bonded complexes, with other calculations. The results of higher level calculations were taken from a recent paper by Benson et al.,[20] which utilized the Stevens effective core potential/valence basis set scheme[21] (augmented with a *d* polarization function on all main-group elements). This level

Table 1. PM3(tm)-Calculated Geometries for Transition-Metal Chlorides versus Experiment

MCl$_3$

M[a]	expt[b,i]	PM3(tm)[c,i]	Δ%[d]	ΔH$_f$[g]	geom[e]	mult[f]	no.[b]
Cu(I)	2.13 ± 0.06	2.25	6	−102.913	TP3	1	2
Cu(II)	*2.22 ± 0.01*	*2.15 ± 0.02*	*3*	*−137.891*	*TP3*	*2*	*1*
Hg(II)	2.42 ± 0.08	2.26	7	−169.522	TP3	1	8

MCl$_4$

M[a]	expt[b,i]	PM3(tm)[c]	Δ%[d]	ΔH$_f$[g]	geom[e]	mult[f]	no.[b]
Cd(II)	2.46 ± 0.03	2.39	3	−178.719	td	1	10
Co(II)	2.27 ± 0.02	2.24	1	−1635.061	td	4	53
Cu(II)	*2.26 ± 0.03*	*2.21*	*2*	*−145.942 (D_{2d})*	*SQP4, td, d2d*	*2*	*94*
Fe(II)	2.18 ± 0.03	2.33	7	−298.429	td	5	7
Fe(III)	2.29 ± 0.05	2.21	3	−334.974	td	6	76
Hg(II)	2.49 ± 0.05	2.34	6	−202.775	td	1	18
Mn(II)	2.36 ± 0.02	2.28	3	−231.873 (C_{2v})	cis divacant	6	13
Mo(II)	*2.28 ± 0.01*	*2.43*	*7*	*5.959 (SQP4)*	*td*	*5*	*1*
Ni(II)	*2.26 ± 0.01*	*2.20*	*3*	*−461.563 (SQP4)*	*td*	*1*	*12*
Pd(II)	2.31 ± 0.04	2.34	1	−151.055 (SQP4)	SQP4	1	18
Zn(II)	2.27 ± 0.02	2.29	1	−214.574	td	1	98

MCl$_5$

M[a]	expt[b,i]	expt[b]	PM3(tm)[c,i]	PM3(tm)[c]	Δ%[d]	ΔH$_f$[g]	mult[f]	no.[b]
Cu(II)	*2.36 ± 0.12*	*SQP5*	*2.26 ± 0.02*	*TBP5*	*4*	*−39.562*	*2*	*1*
			2.26 ± 0.03	SQP5		−39.313		
Hg(II)	2.73 ± 0.37	h	2.46 ± 0.02	TBP5	6	−123.753	1	1
			2.46 ± 0.02	SQP5		−122.790		
Mn(III)	2.29 ± 0.07	SQP5	2.27 ± 0.03	TBP5		−271.843	5	1
			2.25 ± 0.04	SQP5	2	−285.182		
Fe(III)	2.31 ± 0.06	TBP5	2.28 ± 0.06	TBP5	1	−385.257	6	1
			2.29 ± 0.01	SQP5		−379.855		

MCl$_6$

M[a]	expt[b,i]	PM3(tm)[c,i]	Δ%[d]	ΔH$_f$[g]	no.[b]	mult[f]	geom[e]
Cd(II)	2.64 ± 0.08	2.84	8	65.723	2	1	oct
Cr(III)	2.36 ± 0.01	2.29	3	−95.696	1	4	oct
Cu(II)	2.52 ± 0.25	2.34 ± 0.07	7	176.533	8	2	oct
Fe(III)	2.39 ± 0.01	2.36	1	−332.771	3	6	oct
Mo(III)	2.45 ± 0.01	2.45	0	74.198	2	4	oct
Mo(IV)	2.38 ± 0.01	2.39 ± 0.01	0	−6.144	2	3	oct (distorted)
Mo(V)	2.33 ± 0.03	2.35	1	−6.760	2	2	oct
Ni(II)	2.45 ± 0.06	2.34 ± 0.09	4	−133.238	1	3	oct
Pd(IV)	2.42 ± 0.01	2.32	4	−284.656	2	1	oct
Rh(III)	2.35 ± 0.01	2.32	1	−404.254	6	1	oct
Ru(III)	2.37 ± 0.01	2.34 ± 0.05	1	−180.796	1	2	oct
Ru(IV)	2.33	2.29	2	−279.667	1	5	oct
Ta(V)	2.33 ± 0.02	2.30	1	−330.192	12	1	oct
Ti(IV)	2.34 ± 0.02	2.34	0	−596.910	6	1	oct
W(IV)	2.32 ± 0.04	2.28 ± 0.02	2	−368.713	2	3	oct (distorted)
W(V)	2.38 ± 0.01	2.21	76	−436.181	1	2	oct
Zr(IV)	2.47 ± 0.01	2.48	0	−434.623	3	1	oct

[a] M is the metal; the positive oxidation state is indicated by the Roman numeral in parentheses. [b] Experimental averages and standard deviations (both in Å) are taken from data in ref 20; no. is the number examples which were found in ref 20. [c] Calculated bond lengths (in Å) for PM3(tm) minima are given and standard deviations (in cases in which the M−O bond lengths are different due to Jahn−Teller distortions). [d] Δ% = |[(PM3 − expt)/expt]100%|. [e] Coordination geometry of the metal complexes in experiment. Italics denote a discrepancy between the PM3(tm)-predicted metal coordination geometry and that inferred from experiment. TP3: trigonal planar with three ligands. td: tetrahedral. SQP4: square planar for coordination number of 4. TBP5: trigonal bipyramid with five ligands. SQP5: square pyramid with five ligands. d2d: dodecahedral. oct: octahedral. [f] Multiplicity of the complex. [g] Heat of formation in kcal mol^{-1}. [h] The geometry of [HgCl$_5$]$^{3-}$ is between trigonal bipyramid and square pyramid. [i] Average ± standard deviation, Å.

of theory, termed SBK(d), has been extensively and successfully applied to a variety of transition-metal complexes.[22] The wave functions included electron correlation using Møller−Plesset second-order perturbation theory (core electrons not included in the MP2-active space).

RESULTS

1. Chloride Complexes. The main objective of this research is to investigate the predictive ability of the PM3-(tm) method for prototypical ligands encountered in inorganic and organometallic chemistry. The chlorides afford an excellent opportunity for evaluation as they are found in a variety of coordination numbers (three through six are studied here), oxidation states (+2 through +6 in this research), geometries (see below), and transition metals (examples from the Ti through Zn triad were evaluated).[23]

In general, the agreement between PM3(tm)-predicted M−Cl bond lengths and experiments is very good. The

378 *J. Chem. Inf. Comput. Sci., Vol. 39, No. 2, 1999*

CUNDARI AND DENG

Table 2. Hexaaqua Complexes[a]

M	expt	PM3(tm)	Δ%	no.	geom	mult	ΔH_f
Co(II)	2.09 ± 0.03	1.98 ± 0.04	5	12	octahedral	2	−1510.707
Cr(III)	1.96 ± 0.01	1.97	1	1	octahedral	4	477.296
Cu(II)	2.10 ± 0.22	1.96 ± 0.04	7	1	octahedral	2	−53.795
Fe(II)	2.13 ± 0.02	2.00 ± 0.07	6	3	octahedral	5	−205.089
Mn(II)	2.18 ± 0.03	2.12 ± 0.10	3	2	octahedral	6	4.109
Ni(II)	2.05 ± 0.02	1.92	6	11	octahedral	3	−426.140
Zn(II)	2.09 ± 0.03	2.20	6	7	octahedral	1	121.472
			5 av				

[a] For a description of the table headings, see the footnotes to Table 1.

Table 3. Tris(ethylenediamine) Complexes

M	expt	PM3(tm)	Δ%	no.	mult	ΔH_f
Cd(II)	2.37 ± 0.04	2.49	5	9	1	366.202
Co(III)	1.97 ± 0.02	1.97	0	32	1	−1053.138
Cr(III)	2.08 ± 0.02	2.05	1	10	4	543.642
Fe(II)	2.21 ± 0.01	2.08 ± 0.10	6	2	1	−76.731
Ni(II)	2.13 ± 0.01	1.97	7	15	3	−145.441
Rh(III)	2.07 ± 0.01	2.06	0	1	1	291.700
Zn(II)	2.18 ± 0.05	2.21	2	7	1	283.703
			3 av			

[a] For a description of the table headings, see the footnotes to Table 1.

average absolute difference (Δ) for the entire series of 35 chloride complexes is 0.08 Å. To put this number into an appropriate context, the average standard deviation in experimental M−Cl bond lengths for a given metal is ±0.05 Å. The average absolute percent difference (Δ%) in M−Cl bond lengths between experiment and calculation is 3%. Inspection of the data in Table 1 indicates that the poorest results typically involve Cu and Zn triad metal chlorides. It seems that PM3(tm) is especially excellent in predicting the geometries of chlorides from the left-hand side of the series of metal halides, i.e., Δ% = 0% for $[Ti^{IV}Cl_6]^{2-}$, $[Zr^{IV}Cl_6]^{2-}$, and $[Mo^{III,IV}Cl_6]^{3-,2-}$, while $[Ta^VCl_6]^-$ is only 1% different from experiment.

In most cases, the PM3(tm) method is able to predict a lower energy for the coordination isomer observed in the crystallographic experiments. The preference for coordination geometry depends primarily on the metal and its d orbital count for a given ligand. For coordination numbers such as five, the energetic difference between the two polytopes—square pyramidal (SQP5) and trigonal bipyramidal (TBP5)—can be very small. For example, in the case of $[Cu^{II}Cl_5]^{3-}$, the experimental structure is square pyramidal. The PM3-(tm) calculations predict SQP5 $[Cu^{II}Cl_5]^{3-}$ to be ≈ 0.3 kcal mol^{-1} less stable than TBP $[Cu^{II}Cl_5]^{3-}$. For manganese(II) and iron(III) pentachlorides, the PM3(tm) calculations suggest the preference for a particular polytope is more definitive ($\Delta\Delta H_f \geq 5$ kcal mol^{-1}), and here the calculations concur with experiment. For other coordination numbers, the energetic preference for one polytope over another is clear-cut, and thus, the PM3-predicted polytope is generally in agreement with that inferred from X-ray crystallographic analyses.

2. Aqua and Ethylenediamine Complexes. Another important group of complexes in inorganic chemistry are those formed by the coordination of neutral Lewis base ligands to Lewis acidic, d-block metal cations. Water is a prototypical ligand of this type for which a variety of experimental examples are known for several TMs.[23] Additionally, ethylenediamine (en ≡ $H_2NCH_2CH_2NH_2$) is a prototypical nitrogen donor ligand. Coordination number 6, $[M(H_2O)_6]^{q+}$ and $[M(en)_3]^{q+}$ ($q = 2, 3$), was chosen for this study, as this is the most prevalent, Table 2. Additionally, the dominance of a single polytope for six coordination (i.e., octahedral) affords us the opportunity to focus on the ability of PM3(tm) to describe the metal−oxygen and metal−nitrogen linkages.

On average, the absolute differences between PM3(tm)-predicted and experimental M−O bond lengths are 0.10 Å or 5% for seven different hexaaqua complexes, Table 2. The

predictive ability ranges from 1% $[Cr(H_2O)_6]^{3+}$ to 7% $[Cu-(H_2O)_6]^{2+}$. In some cases (depending on the d-orbital population), there is a Jahn−Teller distortion such that instead of six equivalent M−O bond lengths, one observes two set of M−O bond lengths (four short and two long M−O bonds or vice versa). However, in all cases, the geometry about the transition metal is best described as octahedral, in agreement with crystallographic data. Comparison of the data for the aqua and chloride complexes immediately suggests a greater degree of difficulty in describing bonds involving neutral donor ligands.

Tris(en) complexes have four low-energy conformations depending on the orientation of the five-membered ring formed by the metal and the nitrogen and carbon atoms of the chelating ligand. PM3(tm) geometry optimization for the Cr(III) example indicates, as expected, that the M−N bond lengths do not change significantly for the different conformers (Table 3). The metal−nitrogen bond lengths in the PM3-(tm)-optimized structures have generally good agreement with experiment: Δ = 0.07 Å, Δ% = 0% (Co(III) and Rh-(III))−7% (Ni(II)) and Δ% = 3% for the entire set of tris-(en) complexes. It is interesting that the poorest agreement is found for Ni(II)−amine complexes, consistent with the previous results of Adam and co-workers.[14]

3. Multiply Bonded Complexes. Multiply bonded complexes (Table 4), $Cl_nM=E$, were studied for three reasons. First, multiply bonded transition-metal complexes are of great importance.[24] These complexes participated in a variety of catalytically important reactions such as alkane oxidations by oxos[25] and methane activation by imidos.[26] Second, experimental data are widely available for Ta, Zr, and W multiply bonded complexes with main-group elements. Third, high-level calculated geometries are available for these species.[20]

i. Zirconium Complexes. Tetrelide Complexes ($Cl_2Zr=TH_2$; T = C, Si, Ge). All of these complexes are C_1 minima. The PM3(tm)-calculated Zr=C bond length (2.11 Å) is longer than that in the experimental complex (2.02 Å for Zr−alkylidene[27]) by 4%. Since there are no experimental data available for the other Zr−tetrelide multiple bonds, comparison was made between PM3(tm) and SBK(d)/MP2 for the silylene and germylene complexes. Calculated Zr=Ge bonds are similar at the PM3(tm) (2.55 Å) and SBK(d)/MP2 levels (2.54 Å), while the Zr=Si bond in $Cl_2Zr=SiH_2$ is predicted to be shorter in PM3(tm) (2.43 Å) than in SBK-(d)/MP2 (2.52 Å).

Pnictogen Complexes ($Cl_2Zr=PnH$; Pn = N, P, As). The imido complex $Cl_2Zr=NH$ is a C_s minimum (Zr=NH = 172°), and the bond length of Zr=N is in excellent

Table 4. Multiply Bonded Complexes

M/E[a]	sym[b]	MP2[c] Å	PM3(tm)[b] Å	expt[d]	no.[d]	diff PM3/MP2[e]	diff PM3/expt[f]
Zr/CH$_2$	C_1	1.98	2.11	2.02 ± 0.00	1	7	4
Zr/SiH$_2$	C_1	2.52	2.43		0	−4	
Zr/GeH$_2$	C_1	2.54	2.55		0	0	
Zr/NH	C_s	1.83	1.88	1.89 ± 0.05	9	3	−1
Zr/PH	C_1	2.28	2.39	2.53 ± 0.00	1	5	−6
Zr/AsH	C_1	2.37	2.63	2.64 − 2.65	0	11	
Zr/O	C_s	1.78	1.85	1.92 ± 0.08	4	4	−4
Zr/S	C_1	2.23	2.31	2.33 ± 0.01	2	4	−1
Zr/Se	C_s	2.37	2.44	2.48 ± 0.00	2	3	−2
Ta/CH$_2$	C_1	1.92	1.96	2.00 ± 0.09	27	2	−2
Ta/SiH$_2$	C_1	2.40	2.46		0	3	
Ta/GeH$_2$	C_s	2.43	2.45		0	1	
Ta/NH	C_{3v}	1.78	1.77	1.82 ± 0.06	21	−1	−3
Ta/PH	C_1	2.21	2.29	2.32 ± 0.00	1	4	−1
Ta/AsH	C_1	2.31	2.45	2.43 ± 0.00	1	6	1
Ta/O	C_{3v}	1.74	1.75	1.73 ± 0.00	1	1	1
Ta/S	C_{3v}	2.17	2.20	2.19 ± 0.02	2	1	0
Ta/Se	C_{3v}	2.31	2.34	2.34 ± 0.03	3	1	0
W/CH$_2$	C_1	1.86	1.92	2.08 ± 0.14	159	3	−8
W/SiH$_2$	C_1	2.44	2.43		0	0	
W/GeH$_2$	C_s	2.40	2.44	2.59 ± 0.00	1	2	−6
W/NH	C_s	1.75	1.75	1.77 ± 0.06	135	0	−1
W/PH	C_1	2.2	2.19	2.23 ± 0.07	2	0	−2
W/AsH	C_1	2.29	2.37	2.35 − 2.39	0	3	
W/O	C_s	1.73	1.75	1.72 ± 0.05	169	1	2
W/S	C_{4v}	2.16	2.13	2.15 ± 0.05	42	−1	−1
W/Se	C_{4v}	2.3	2.27	2.35 ± 0.05	15	−1	−3

[a] M is the metal, and E is the ligand. [b] Calculated bond lengths (in Å) and symmetries for PM3(tm) minima are given. [c] Calculated bond lengths (in Å) using SBK(d)/MP2 calculations. [d] Experimental averages and standard deviations (both in Å) are taken from data in ref 20; no. is the number of examples which were found in ref 20. [e] Diff % = [(PM3 − MP2)/MP2]100%. [f] Diff % = [(PM3 − expt)/expt]100%.

agreement with the experimental estimates (1.88 Å (PM3-(tm)): 1.89 ± 0.05 Å (experiment, nine examples). The complexes Cl$_2$Zr=PH and Cl$_2$Zr=AsH form C_1 minima. Unlike the imido, the Zr=PnH groups (Zr=PH = 71°; Zr=AsH = 44°) in these minima are decidedly bent instead of linear. The optimized Zr=Pn bond lengths are longer with PM3(tm) than those determined with the SBK(d)/MP2 scheme (average difference = 6%), Table 4.

Chalcogenide Complexes (Cl$_2$Zr=Ch; Ch = O, S, Se). The chalcogenides Cl$_2$Zr=O and Cl$_2$Zr=Se are C_s minima, while Cl$_2$Zr=S is a C_1 minimum. The semiempirical results agree very well with experiment. The Zr=Ch bonds obtained by PM3(tm) calculation are slightly shorter on average by only 2% as compared to experimental estimates. The biggest difference (4%) is observed for Cl$_2$Zr=O−1.85 Å (PM3-(tm)) versus 1.92 Å (expt)—although this is reasonable since the standard deviation in experimental Zr=O bond lengths is ±0.08 Å. The average experimental Zr=O bond length is closer to the PM3-calculated results than SBK(d)/MP2 (1.78 Å), Table 4.

ii. Tantalum Complexes. Tetrelide Complexes (Cl$_3$Ta=TH$_2$). The complex Cl$_3$Ta=GeH$_2$ is a C_s minimum, while its other congeners are C_1 minima. The PM3-calculated bond length of Ta=C (1.96 Å) is only 0.04 Å (2%) shorter than the experimental average (2.00 ± 0.09 Å) of 27 complexes. Furthermore, when the PM3(tm) multiple bond lengths are compared with the SBK(d)/MP2 values, the results are very similar, Table 4.

Pnictogen Complexes (Cl$_3$Ta=PnH). Cl$_3$TaNH is a C_{3v} minimum; Cl$_3$TaPH and Cl$_3$TaAsH are C_1 minima. Compared with experiment, the bond length difference for Ta=N is

0.05 Å (1.77 Å (PM3), 1.82 ± 0.06 Å (expt, 21 examples)) and 0.03 Å for Ta=P (2.29 Å (PM3), 2.32 Å (expt, 1 example)). The PM3(tm)-calculated Ta=As bond length (2.45 Å) is larger than the SBK(d)/MP2 result (Δ% = 6%) but in agreement with experiment (2.43 Å).

Chalcogenide Complexes (Cl$_3$Ta=Ch). These complexes are all C_{3v} minima. Agreement between PM3(tm) and experiment is excellent (Δ% = 0% for Ta=S and Ta=Se, 1% for Ta=O), Table 4. The high accuracy of SBK(d)/MP2 and PM3(tm) suggests that both methods are appropriate to model chalcogenido complexes, except in the case of complexes containing fifth period main-group elements[28] for PM3(tm) (Δ% = 17% for Ta=Te).

iii. W Complexes. Tetrelide Complexes (Cl$_4$W=EH$_2$). The germylene Cl$_4$W=GeH$_2$ is a C_s minimum, while the others are C_1 minima. The average bond length of W=C in experiment is 2.08 Å with a standard deviation of 0.14 Å (159 examples). Hence, the PM3(tm)-calculated value for Cl$_4$W=CH$_2$ (1.92 Å) is toward the short end of W−carbenes reported in the Cambridge database[23] (range for W=C = 1.82−2.32 Å) but is closer to the experimental average than the SBK(d)/MP2 value (1.86 Å). The bond length of W=Ge in Cl$_4$WGeH$_2$ is 2.40 (SBK(d)/MP2) and 2.44 Å (PM3-(tm)) as compared to 2.59 Å for an experimental example.[29] Though the difference between PM3(tm) and experimental bond lengths may be large, the PM3(tm)-calculated difference in W=C and W=Ge bond lengths (0.52 Å) is nearly identical to the experimental difference (0.51 Å), Table 4.

Pnictogen Complexes (CL$_4$W=PnH). The complex Cl$_4$W=NH is a C_s minimum, and the others are C_1 minima. Both calculations show great agreement with experiment:

W≡N (1.75 Å (PM3(tm) and SBK(d)/MP2), 1.77 ± 0.06 Å (expt, 135 examples)); W≡P (2.20 Å (MP2), 2.19 Å (PM3), 2.23 ± 0.07 Å (expt, 2 examples), Table 4. Additionally, SBK(d)/MP2 and PM3-predicted multiple bond lengths are consistent with each other for all W−Pnictogen complexes (Δ% < 3%).

Chalcogenide Complexes (CL₄W=Ch). The oxo Cl_4WO is a C_s minimum, while Cl_4WS and Cl_4WSe are C_{4v} minima. PM3(tm)-calculated W=Ch bond lengths agree with experimental averages. The differences between them are 2% (W= O), 1% (W=S), and 3% (W=Se), Table 4. The SBK(d)/ MP2 approach also gives good results and is more accurate than PM3(tm) for W=Te compounds.[28]

From the study of Zr, Ta, and W multiply bonded complexes with main-group 14, 15, and 16 elements, the following important points have emerged. First, PM3 is successful in predicting transition-metal−main-group multiple bonds. Comparison of 18 complex types for which structural data are experimentally available was made with PM3(tm). The absolute average percent difference is only 2%. In only five cases do PM3(tm) multiple bond lengths (W=C, Δ% = 8%; W=Ge, Δ% = 6%; Zr=C, Δ% = 4%; Zr=P, Δ% = 6%, Zr=O, Δ% = 4%) differ from experiment by >3%. Among them, Zr=O and W=C are reasonable since they fall within the range of the experimental bond length standard deviations (0.08 and 0.14 Å, respectively). Second, the predictive ability of PM3(tm) is competitive with SBK(d)/MP2 calculations for all main-group elements except those of the fifth period, Δ% = 4% for SBK(d)/MP2 versus experiment with 8 out of 18 bond types having Δ% > 3%. This is especially important given the large computational savings that are obtained when employing PM3(tm) semiempirical calculations.

4. Organometallics. Organometallic complexes represent, along with coordination complexes like those studied above, the second major family of d-block complexes. Organometallic complexes are for considerable interest in catalysis[1] (olefin polymerization by organozirconium complexes is just one of many examples), and hence, an assortment of 19 d-block complexes were investigated. Each complex contains the cyclopentadienyl ligand given its importance in organotransition-metal chemistry. The comparison of PM3(tm)-calculated and experimental geometries for the inner coordination sphere is organized in Table 5. As is evident from Table 5, the PM3(tm) method performs exceptionally well for the organometallic complexes studied. For all metric parameters investigated (41 metal−ligand bond lengths and 51 ligand−metal−ligand bond angles), the average absolute difference between PM3(tm) and experiment is 2%. This same excellent level of agreement is seen for both bond lengths and bond angles (average Δ% = 2% for each). The biggest theory−experiment differences are 7% for the Ni−N bond lengths and 9% for the N−Ni−N bond angle in CpNi-(bipyridine). The poor results observed for the Ni complex are consistent with the calculations described above for Ni-(II) coordination complexes and the work of Adam et al.[14] Of the 41 bond lengths and 51 angles investigated, there are only 4 and 6, respectively, with theory−experiment differences of more than 4% (see Table 5). Hence, apart from nickel, the PM3(tm) method seems to be a very attractive technique for prediction of the geometry of organometallics.

Table 5. Experimental[20] and PM3(tm) Bond Lengths (Å) and Bond Angles (deg) for Organometallics

	X-ray	PM3	Δ%		X-ray	PM3	Δ%
Cp₂Ti(CH₃)₂				**CpRu(CO)₂Br**			
Ti−Cp	2.08	2.10	1	Ru−Br	2.54	2.53	0
Ti−CH₃	2.18	2.11	3	Ru−CO	1.87	1.88	1
Cp−Ti−Cp	135	132	2	Ru−Cp	1.88	1.81	4
Cp−Ti−CH₃	106	106	0	Br−Ru−Cp	123	123	0
H₃C−Ti−CH₃	91	95	4	Cp−Ru−CO	126	128	2
				Br−Ru−CO	90	89	1
CpMn(CO)₂(=CMe₂)				OC−Ru−CO	91	92	1
Mn−Cp	1.83	1.88	3				
Mn−CO	1.80	1.76	2	**CpFe(CO)₂Cl**			
Mn−C	1.87	1.81	3	Fe−Cp	1.71	1.77	4
Cp−Mn−CO	124	122	2	Fe−CO	1.77	1.74	2
CO−Mn−CO	89	88	1	Fe−Cl	2.29	2.22	3
CO−Mn−CH	91	93	3	Cp−Fe−CO	124	126	2
Cp−Mn−CH	128	128	0	CO−Fe−CO	94	95	1
				Cl−Fe−CO	91	91	0
CpCo(CO)₂				Cl−Fe−Cp	123	119	3
Co−Cp	1.66	1.72	4				
Co−CO	1.74	1.75	1	**Cp₂Hf(CH₃)₂**			
Cp−Co−CO	133	134	1	Hf−Cp	2.21	2.24	1
CO−Co−CO	94	93	1	Hf−CH₃	2.29	2.2	4
				Cp−Hf−Cp	133	131	1
CpMo(CO)₃				Cp−Hf−CH₃	106	105	0
Mo−Cp	2.05	2.08	1	CH₃−Hf−CH₃	96	102	7
Mo−CO	1.91	1.88	2				
Cp−Mo−CO	127	126	1	**Cp₂Zr(CH₃)₂**			
OC−Mo−CO	88	88	0	Zr−Cp	2.23	2.23	0
				Zr−CH₃	2.28	2.29	0
Cp₂ W(=C(H)Ph)				Cp−Zr−Cp	133	133	0
W−Cp	1.96	1.97	1	Cp−Zr−CH₃	106	106	0
W=C	2.05	2.10	2	CH₃−Zr−CH₃	96	93	3
Cp−W−Cp	143	146	2				
Cp−W=C	108	103	5	**CoCp₂⁺**			
				Co−Cp	1.62	1.7	5
CpNi(bipy)				Cp−Co−Cp	179	180	1
Ni−N	1.96	1.82	7				
Ni−Cp	1.84	1.79	3	**Cp₂RuCl⁺**			
N−Ni−N	82	89	9	Ru−Cl	2.42	2.33	4
N−Ni−Cp	139	135	3	Ru−Cp	1.86	1.82	2
				Cp−Ru−Cp	146	154	5
Cp₂Ti(oxalate)				Cp−Ru−Cl	107	103	4
Ti−O	2.00	1.94	3				
Ti−Cp	2.05	2.04	0	**FeCp₂**			
O−Ti−O	79	83	5	Fe−Cp	1.66	1.68	1
Cp−Ti−O	108	107	1	Cp−Fe−Cp	179	180	1
Cp−Ti−Cp	133	133	0				
				Cp₂Ta(Cl)(=C(H)ᵗBu)			
Cp₂Ta(H)CO				Ta−Cp	2.11	2.13	1
Ta−CO	2.04	2.16	6	Ta−Cl	2.45	2.36	4
Ta−Cp	2.04	2.06	1	Ta=CH	2.03	2.01	1
Cp−Ta−Cp	144	148	3	Cp−Ta−Cp	130	130	0
Cp−Ta−CO	104	105	1	Cp−Ta−Cl	105	103	2
				Cp−Ta=CH	109	110	1
CpMn(CO)₂				Cl−Ta=CH	98	92	6
Mn−Cp	1.78	1.86	5				
Mn−CO	1.79	1.77	1	**Cp₂Ta(=CH₂)(CH₃)**			
Cp−Mn−CO	124	124	0	Ta−Cp	2.10	2.12	1
CO−Mn−CO	92	92	0	Ta=CH₂	2.04	2.00	2
				Ta−CH₃	2.27	2.22	2
Cp₂Mo(CH₂)₄				Cp−Ta−Cp	136	136	0
Mo−C	2.27	2.19	4	Cp−Ta−CH₃	103	104	1
Mo−Cp	1.98	2.01	2	Cp−Ta=CH₂	106	106	0
C−Mo−C	75	75	0	CH₃−Ta=CH₂	96	93	3
C−Mo−Cp	106	108	2				
Cp−Mo−Cp	139	135	3				

SUMMARY AND CONCLUSION

This paper reports the calculation of around 100 compounds involving all transition metals for which the parameters are available in PM3(tm). We found that, in general, PM3(tm)-predicted geometries agreed with experimental data very well; the average absolute difference (Δ%) in bond

PM3(TM) ANALYSIS OF TRANSITION-METAL COMPLEXES

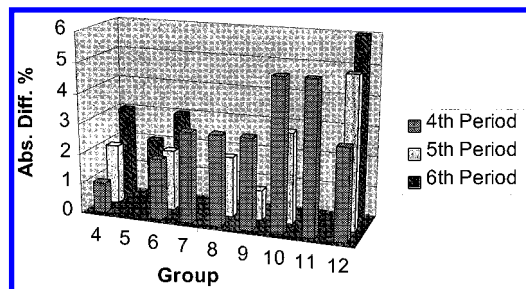*J. Chem. Inf. Comput. Sci., Vol. 39, No. 2, 1999* **381**

Figure 1. Plot of the absolute value of the average percent differences ($\Delta\%$) between the calculated and experimental bond lengths for the transition metals parameterized with PM3(tm).
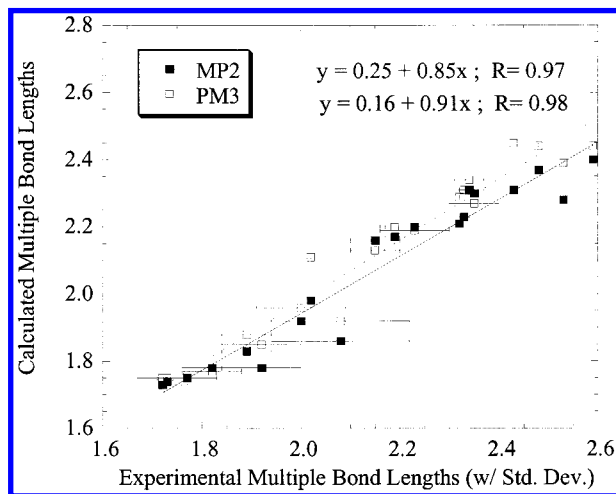

Figure 2. Comparison of the experimental and calculated multiple bond lengths (in Å) determined at the PM3(tm) and MP2/SBK(d) levels of theory.

lengths versus experiment for all tested complexes is only 3%. An overview of the $\Delta\%$ distribution as a function of position in the periodic table is shown in Figure 1. This figure indicates that the predictive ability is excellent from group 4 to 9 (average $\Delta\% = 2\%$) but diminishes from the Ni triad (group 10) toward the right side (average $\Delta\% = 5\%$) of the transition series. Comparing different types of complexes, we found that the best result was obtained for multiply bonded complexes; the accuracy (average $\Delta\% = 2\%$) in PM3(tm)-predicted bond lengths is competitive with higher level SBK(d)/MP2 calculations for all main-group elements except those of the fifth period. Indeed, plotting the data, Figure 2, shows the PM3(tm) method to be closer to ideal, i.e., a least-squares line with slope and correlation coefficient closer to unity and an intercept closer to zero. Hence, the results of this research indicate that the PM3(tm) method is competent for structural prediction of many families of TM

complexes at considerably reduced computational times compared to ab initio techniques. The predictive ability does, however, seem to degrade for some of the metals from the later portion of the transition series. Thus, a reinvestigation of their PM3(tm) parameters may be in order.

REFERENCES AND NOTES

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley, New York, 1988.
(2) Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.
(3) Martins, J. B. L.; Longo, E.; Andres, J.; Taft, C. A. *THEOCHEM* **1995**, *335*, 167.
(4) Martins, J. B. L.; Andres, J.; Longo, E.; Taft, C. A. *Int. J. Quantum Chem.* **1996**, *57*, 861.
(5) Martins, J. B. L.; Longo, E.; Andres, J.; Taft, C. A. *THEOCHEM* **1996**, *363*, 249.
(6) Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 221.
(7) Anders, E.; Koch, R.; Freunscht, P. *J. Comp. Chem.* **1993**, *14*, 1301.
(8) Furuki, T.; Sakurai, M.; Inoue, Y. *J. Comp. Chem.* **1995**, *16*, 378.
(9) Poleshchuk, O. Kh.; Koput, J.; Latosinska, J. N.; Nogaj, B. **1996**, *380*, 267.
(10) Poleshchuk, O. Kh.; Latosinska, J. N.; Nogaj, B. J. *J. Mol. Struct.* **1996**, *380*, 277.
(11) Dannenberg, J. J. *THEOCHEM* **1997**, *401*, 279.
(12) Csonka, G. I.; Angyan, J. G. *THEOCHEM* **1997**, *393*, 31.
(13) Dos Santos, H. F.; De Almeida, W. B. *THEOCHEM* **1995**, *335*, 129.
(14) Adam, K. R.; Atkinson, I. M.; Lindoy, L. F. *J. Mol. Struct.* **1996**, *384*, 183.
(15) Børve, K. J.; Jensen, V. R.; Karlsen, T.; Støvneng, J. A.; Swang, O. *J. Mol. Model.* **1997**, *3*, 193.
(16) Decker, S. A.; Donini, O.; Klobukowski, M. *J. Phys. Chem. A* **1997**, *101*, 8734.
(17) Cundari, T. R.; Saunders, L. C.; Sisterhen, L. L. *J. Phys. Chem. A* **1998**, *102*, 997.
(18) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294.
(19) Stewart, J. J. P. *J. Comp-Aided Mol. Des.* **1990**, *4*, 1.
(20) Benson, M. T.; Cundari, T. R.; Li, Y.; Strohecker, L. A. *Int. J. Quantum Chem., Sanibel Symp.* **1994**, *28*, 181.
(21) Krauss, M.; Stevens, W. J.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612.
(22) Cundari, T. R.; Gordon, M. S. *Coord. Chem. Rev.* **1996**, *147*, 87.
(23) Experimental data were obtained from the Cambridge Structure Database System, V5.13 (Allen, F. H.; Kennard, O. *Chem. Des. Autom. News* **1993**, *8*, 31).
(24) Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988.
(25) *Cytochrome P-450;* Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.
(26) Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1993**, *32*, 131.
(27) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336.
(28) Cundari, T. R.; Deng, J. Unpublished results.
(29) Petz, W. *Chem. Rev.* **1986**, *86*, 1019.

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