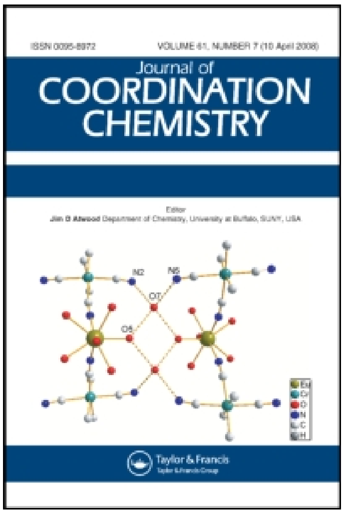

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De novo prediction of the ground state structure of transition metal complexes using semiempirical and *ab initio* quantum mechanics. Coordination isomerism

Corneliu Buda[a]; Alondra Flores[b]; Thomas R. Cundari[a]
[a] Department of Chemistry, University of North Texas, Denton, TX 76203, USA [b] Department of Chemistry, University of Texas at Brownsville, Brownsville, TX 78520, USA

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De novo prediction of the ground state structure of transition metal complexes using semiempirical and *ab initio* quantum mechanics. Coordination isomerism

CORNELIU BUDA†, ALONDRA FLORES‡ and THOMAS R. CUNDARI†*

†Department of Chemistry, University of North Texas, Denton, TX 76203, USA
‡Department of Chemistry, University of Texas at Brownsville, Brownsville, TX 78520, USA

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The ground state coordination isomers for 30 different trigonal bipyramidal transition metal complexes have been predicted using different levels of quantum mechanics: semiempirical (PM3(tm)), *ab initio* (MP2//HF), pure (BPW91) and hybrid (B3PW91) density functional theory (DFT) methods. For species where these methods failed to reproduce crystallographic data, hybrid quantum mechanics/molecular mechanics (QM/MM) methods were used to study more exact experimental models. Literature deficiencies regarding ground state multiplicity of these species were supplemented by spin predictions using previously tested PM3(tm) methods. Geometry optimization calculations were performed for each possible coordination isomer. The predicted ground state minima provided by the different methods are compared to each other and with crystallographic data. Pure DFT functionals outperformed hybrid functionals and MP2//HF. The very rapid PM3(tm) parameterization method provided accurate predictions in comparison to other levels of theory. An integrated MM/PM3(tm)/DFT *de novo* scheme accurately reproduced crystallographic data for species where the individual methods failed.

Keywords: Theoretical; Transition metal complexes; Semiempirical; *Ab initio* quantum mechanics

1. Introduction

One of the most important characteristics of a transition metal compound is the number of ligands bonded to the central metal; this quantity is known as the coordination number (CN). A broad range of coordination numbers (examples from $CN = 1$ to 12 are routinely accessible depending on the ionic radius and d orbital count of the metal) is found for transition metal species, providing a rich variety of oxidation states and large structural and chemical diversity, and there are many important applications, including biological and industrial catalysis [1].

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*Corresponding author. Email: tomc@unt.edu

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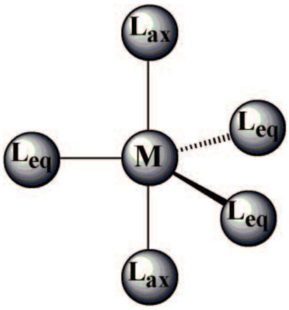


Scheme 1.

From all the possible coordination numbers, the present research focused on five coordination (CN = 5). A specific structural polytope, trigonal bipyramidal (TBP5), was selected for consideration. The most common structural isomers of five-coordinate complexes are square pyramidal (SQP5) and TBP5, the latter being chosen for this research based on the large amount of crystallographic data available in the Cambridge Structural Database (CSD) necessary to evaluate very rapid approximate modeling techniques for transition metal chemistry [2]. In practice, a whole spectrum of intermediate ML_5 geometries arises from SQP5 → TBP5 pathways, such as the Berry pseudorotation process, which typically show low energy barriers (often less than 10 kcal/mol) for the majority of ML_5 complexes [3]. For TBP5 complexes, there are two inequivalent coordination sites around the central metal atom, equatorial (*eq*) and axial (*ax*) [4] (scheme 1).

Ground state geometry prediction for transition metal complexes, which is always very challenging, is further complicated for TBP5 species because of the presence of inequivalent *ax* and *eq* coordination sites. Ligand coordination site preferences (*ax* versus *eq*) depend on factors such as the number of electrons located in d orbitals of the transition metal, as well as electronic and steric effects brought about by the ligands. Rossi and Hoffmann [5] tested the preferences for different coordination isomers using the extended Hückel method. They concluded that the M–L bond in the *eq* site is stronger for a σ-donor ligand when the metal has d^n ($n = 1$–$4, 10$) electrons, and weaker for $n = 8$. Subsequently, Shustorovich [6] used the same theoretical approach to calculate the ratios of overlap population *eq*/*ax* for ns, np and (n − 1)d orbitals. He concluded that $d^{0–4}$ electron configurations afford more stable bonds for the *eq* site, and d^8 for the *ax* site. For d^8 and d^9 TBP5 complexes, Burdett [7], using an angular overlap model, established that the $M–L_{ax}$ bonds are more stable than the $M–L_{eq}$ bonds, even when the same ligand is involved.

Ligand characteristics were indicated to be important for position around the central transition metal in IR and NMR studies applied to 18-electron $HRh(CO)_2(phosphine)_2$ species by Bregman *et al.* [8]. The ligand *eq*–*eq* versus *ax*–*eq* ratio was strongly dependent on diphosphine basicity and bite angle. Using the same experimental methods in conjunction with density functional theory (DFT) calculations, van der Veen *et al.* [9] concluded that upon decreasing the basicity of ligands (e.g. phosphines), the *eq*–*eq* coordination isomer will be preferred over the *ax*–*eq* isomer. Casey *et al.* [10] stated that the ground state coordination isomer is not affected by steric effects for identical ligands situated in various coordination sites (e.g. *eq*–*eq* and *ax*–*eq*) after performing

MM (molecular mechanics) calculations on $HRh(CO)_2(phosphine)_2$ species, but can be influenced by modifying the electronic effect of ligands by adding/removing electron-withdrawing substituents.

The speed and lower cost of computational chemistry has made it an attractive option when there are insufficient experimental data. For example, a new force field was developed based on experimental data and applied to Osborn carbenes [11] and the results (e.g. carbenes preferred the *eq* coordination site) were supported by *ab initio* and experimental data. A new conformational search algorithm was developed by Leach [12] to find the most stable coordination isomer for transition metal complexes. This protocol reproduced the experimental values for Cu and Co complexes, but not for Pd.

The advantages of highly correlated methods were revealed by Lüthi *et al.* [13], while Hartree–Fock (HF) calculations show large differences for *ax* and *eq* Fe–C bonds in $Fe(CO)_5$, but when increasing the treatment of electron correlation using contracted configuration interaction (CCI), only small differences were observed. Using highly correlated methods, such as complete active space self-consistent field (SCF) (CASSCF) and CAS second-order perturbation theory (CASPT2), Matsubara *et al.* [14] calculated possible excited state isomerization pathways for $M(CO)_4L$ species.

Even though calculations have covered specific areas of TBP5 transition metal complexes, there is, to our knowledge, no comprehensive computational study of coordination isomerism using modern quantum chemical methodologies. The goal of this research was to test the performance of semiempirical quantum mechanics (SEQM), *ab initio* and DFT calculations for a diverse assortment of ligands and transition metals. Specifically, we aimed to assess the reliability of very fast SEQM methods in predicting the ground state coordination isomer, so as to further assess their reliability in a *de novo* design protocol for transition metal complexes [15]. Similar efforts involving other types of isomerism have been presented for geometric [15], 'spin' [16] and structural [17] isomers.

2. Computational methods

Our goal was to compare the ability to predict the appropriate ground state coordination isomer by using PM3(tm), an SEQM method that uses a minimal valence basis set of Slater-type orbitals [18], with more advanced and time-consuming *ab initio* methods represented by MP2//HF (geometry optimization with HF, followed by single point calculation using Møller–Plesset second-order perturbation theory, MP2) and DFT methods exemplified by pure (BLYP, BPW91) and hybrid (B3LYP, B3PW91) functionals. All *ab initio* and DFT methods used the CEP-31G valence basis set [19], using d polarization functions for all 'p' block elements. The CEP-31G basis set is double-zeta for main group elements and valence triple-zeta for transition metals [19]. The extra basis functions for 'p' block elements were represented by a polarization function (ζ_d) obtained from the 6-31+G* basis set ($Cl = 0.75$; $P = 0.55$; $S = 0.65$; $Si = 0.45$; $C,N,O = 0.8$), the 6-311G* basis set ($As = 0.264$; $Br = 0.451$; $I = 0.302$) or the LANL2DZdp effective core potential basis set ($Sn = 0.186$) [20].

The 'B' functionals include Slater [21] local and Becke [22] non-local exchange, while the 'B3' functionals are formed from Slater + HF local and Becke [22] non-local exchange, along with Vosko, Nusair, Wilk [23] local correlation. The 'LYP' functionals contain the Lee, Yang, Parr [24] correlation functional, while the designation 'PW91' denotes the 1991 non-local correlation functional developed by Perdew and Wang [25].

This research used the PM3(tm) method as implemented in the Spartan'04 [26] package, while for all *ab initio* and DFT calculations the Gaussian'03 [27] program was used.

3. Results and discussion

This research entails calculations for 30 different TBP5 complexes chosen to be representative of structurally characterized transition metal complexes as determined by a survey of the CSD [2]. Ligand dissimilarities confer five unique structural classes, each one including a different number of possible coordination isomers (*n*): MA_4B (2), MA_3B_2 (3), MA_3BC (4), MA_2B_2C (5), MA_2BCD (7), where A, B, C and D denote ligands.

3.1. *Geometry prediction protocol*

All 30 TBP5 complexes were selected from a large variety of geometries available in the CSD [2] attempting to cover all five structural classes ($MA_4B, MA_3B_2, MA_3BC, MA_2B_2C, MA_2BCD$). The number of complexes within each coordination isomer class was chosen with regard to the possible number of coordination isomers (10 MA_4B complexes with two coordination isomers, four MA_2BCD with seven isomers, etc.). The model geometries contained a large variety of ligands connected to the central transition metal by multiple (=O, =NH, $=CH_2$) or single/dative bonds (AH_3, where $A = C, Si, Sn, N, P, As$; AH, where $A = O, S$; and F, Cl, Br, I). Some of the bulky ligands (M–L–R) were truncated to M–L–H, to ameliorate the cost of very expensive *ab initio* and DFT calculations. This simplification was necessary to complete the higher level calculations within a reasonable time period and to extend the number of investigated structures to as many different TBP5 configuration isomer classes as possible. The size of the models studied ranged between a maximum of 20 atoms (223 basis functions) and a minimum of 11 atoms (106 basis functions).

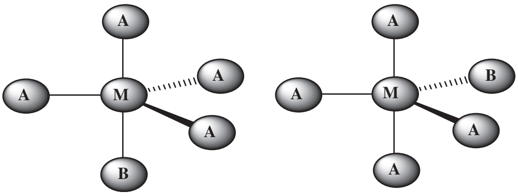
All possible coordination isomers, corresponding to each specific TBP5 class [10 species of MA_4B type, each with two possible coordination isomers, 6 MA_3B_2 (3), 5 MA_3BC (4), 5 MA_2B_2C (5) and 4 MA_2BCD (7)] were built from scratch using graphical interfaces provided by the packages used [26,27]. In total, 111 coordination isomers were constructed and used as initial guesses for geometry optimization. Each of these calculations followed the same protocol, consisting of energy minimization followed by analytical frequency calculations. In some cases after the first stage of geometry optimization, not all stationary points were true minima. In these circumstances, in a second step, the optimized structure was distorted along the vibrational mode with the highest imaginary frequency, and geometry optimization performed and frequencies calculated again. This process was repeated until no imaginary frequencies were obtained for the lowest energy structure.

The lack of experimental data regarding spin states for many reported TBP species, combined with the high accuracy provided by SEQM methods [16], required additional calculations using the PM3(tm) Hamiltonian to determine the appropriate ground state multiplicity for each complex. Single point calculations were performed for the crystallographic geometry at all possible low-, intermediate- and high-spin states to find the

Table 1. Theoretical results compared with crystallographic data.

Species	B3PW91		B3LYP		BPW91		BLYP		HF//MP2		PM3(tm)	
	R	W	R	W	R	W	R	W	R	W	R	W
MA_4B	9	1	9	1	8	2	9	1	9	1	8	2
MA_3B_2	6	0	6	0	6	0	6	0	4	2	5	1
MA_3BC	3	2	3	2	4	1	4	1	5	0	3	2
MA_2B_2C	4	1	4	1	5	0	4	1	4	1	5	0
MA_2BCD	4	0	4	0	4	0	4	0	4	0	3	1
Total	26	4	26	4	27	3	27	3	26	4	24	6
% Right	87		87		90		90		87		80	

R = right (i.e. prediction agrees with experimental crystal structure); W = wrong prediction.



Scheme 2. MA_4B.

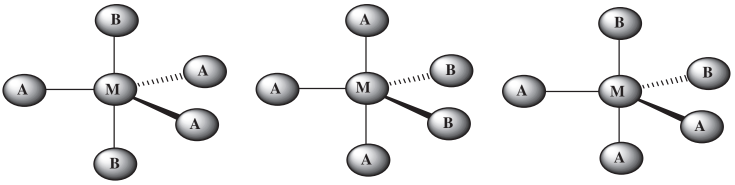
most stable spin state. The subsequent geometry optimizations (semiempirical and *ab initio*) were performed at the lowest energy spin state thus found by PM3(tm).

Theoretical results for the different coordination isomers for all 30 different transition metal complexes were compared to each other, and to the crystallographic data [2]. These results are summarized below.

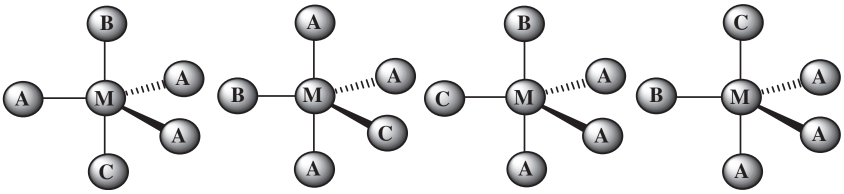
3.2. *Comparison of SEQM and ab initio methods with crystallographic data*

If the predicted geometry had the same disposition of ligands as the crystal structure with regard to coordination site (*ax*/*eq*), the right (R) answer (otherwise wrong (W)) was recorded for each computational method, and the results were collated for every class of TBP5 complex (table 1).

All 10 complexes in the MA_4B coordination isomer group (scheme 2) have a singlet spin state as determined by PM3(tm). For five complexes, FOGPUM [28] $[Fe(CO)_4\{Si(O^tBu)_2(OP(NMe_2)_3\}]$, GERYUX [29] $[Fe(CO)_4\{P(SiMe_3)_3\}]$, JEBNIN [30] $[Co(CO)_4(CH_2SF_6)]$, NUYWUZ [31] $[Fe(CO)_4\{C(CHP(NMe_2)_3)(OCH_3)\}]$, and TAYPAK [32] $[Fe(CO)_4(CCP\text{-}(NMe_2)_2\text{-}CH_2PO(NMe_2)_2]$, all six computational methods predicted the unique 'B' ligand to be situated in the *ax* position, thus matching the experimental crystallographic data. Non-DFT methods (MP2//HF and PM3(tm)) situated the arsine ligand in the *ax* position for CAJZOC [33] $[Ru(CO)_4\{AsPh_3\}]$, reproducing experimental observations, whereas DFT methods predicted more stable *eq* coordination for the arsine compared with the *ax* site: $\Delta E_{ax\text{–}eq} = 0.42$ (B3PW91), 0.66 (B3LYP), 0.36 (BPW91), 0.72 kcal/mol (BLYP). All of the theoretical methods accurately predicted the *ax* coordination isomer to be more stable for DTHFEC [34] $Fe(CO)_4$(1,3-dithiane), except for BPW91, where the *eq* isomer was calculated to be more stable than *ax* by 0.30 kcal/mol. Despite the similarity among the DFT methods and the experimentally observed data, MP2//HF incorrectly predicted the *ax* isomer



Scheme 3. MA_3B_2.



Scheme 4. MA_3B_C.

to be more stable ($\Delta E_{ax-eq} = 30.66$ kcal/mol) for FONTAD [35] [$Mn(CO)_4NO$], while PM3(tm) predicted more stable *eq* isomers ($\Delta E_{ax-eq} = 2.25$ kcal/mol) for MCINIF [36] [$Fe(CO)_4NMe((CH)_3Ph)$] and ($\Delta E_{ax-eq} = 2.50$ kcal/mol) PYDTCI [37] [$Fe(CO)_4py$], both in disagreement with experiment.

For the 10 species that comprise the MA_4B class, MP2//HF, hybrid functionals (B3PW91, B3LYP) and one of the pure functionals, BLYP, reproduced the crystallographic coordination isomers in nine out of 10 cases, while BPW91 and PM3(tm) replicated experimental data for eight out of 10 species (table 1).

For BRURMN [38] [$MnBr_2(OC(NHCH_3)_2)_3$] (sextet, both 'B' ligands situated in *eq–eq* positions), CBFMOP [39] [$Fe(CO)_3(P(OMe)_3)_2$] (singlet, *ax–ax*), CEZKIB [40] [$Ru(CO)_3(PPh_3)_2$] (singlet, *ax–ax*), and CLTAMV [41] [$VCl_3(NMe_3)_2$] (triplet, *ax–ax*), all theoretical methods correctly predicted the coordination isomers (scheme 3). Crystallographic coordination isomers were reproduced by all theoretical methods for CPETCP [42] [$CoCl_3(PEt_3)_2$] (triplet, *ax–ax*) and IMPONI [43] [$NiI_2(P(OMe)_3)_3$] (singlet, *eq–eq*), except for MP2//HF, where both predicted geometries are four coordinate with a dissociated phosphine ligand.

Summarizing the results for the MA_3B_2 class, all DFT methods reproduce crystallographic data for all six species, outperforming PM3(tm) with five out of six, and MP2//HF with just four out of six appropriate coordination isomers (table 1).

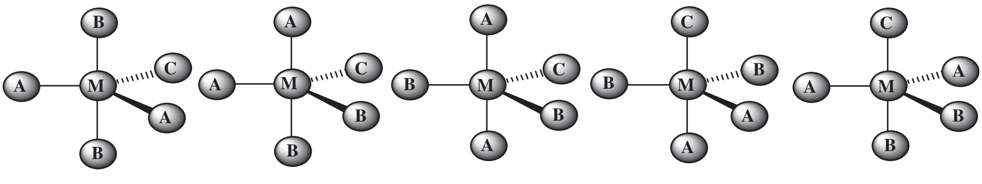
Agreement between experimental and all theoretical methods was found for the MA_3BC complexes (scheme 4) JEGDOO [44] [TcCl(NO)(2,3,5,6-tetramethylbenzene-thiolato-S)$_3$] (singlet, *ax–ax* for Cl and NO) and MSIPMO20 [45] [$MoCl(PMe_3)(CH_2SiMe_3)_3$] (triplet, *ax–ax*). The less expensive methods MP2//HF and PM3(tm) provided a proper description with regard to coordination sites for CAFKOJ [46] [$Ir(CO)(CH_2SiMe_3)(P(OMe)_3)_3$] (singlet, *ax–eq*), while the expensive DFT methods predicted the *ax–ax* coordination isomer to be more stable than *ax–eq*: B3PW91 (1.23 kcal/mol), B3LYP (1.20 kcal/mol), BPW91 (0.78 kcal/mol), BLYP (0.65 kcal/mol). For LIPKOK [47] singlet [$TaCl(Si(SiMe_3)_3)(NMe_2)_3$], all methods reproduced the experimentally observed *ax–eq* coordination isomer (*ax* Cl and *eq* $Si(SiMe_3)_3$), with the exception of PM3(tm), where the *ax–ax* isomer is predicted to be lower in energy than the *ax–eq* isomer by 3.83 kcal/mol. An assortment of results was obtained for RASQUX [48] singlet [$Co(CO)_3(CF_3)(PPh_3)$], where pure (BPW91, BLYP) functionals and MP2//HF provide a proper *ax–ax* disposition of the 'B' and 'C' ligands, while hybrid (B3PW91, B3LYP) functionals and PM3(tm) predicted the *ax–eq* coordination isomer to be more stable than the *ax–ax* isomer by 0.50, 0.26 and 1.36 kcal/mol, respectively.

For the MA_3BC class of species MP2//HF replicates crystallographic data for all five species, while pure functionals (BPW91, BLYP) successfully predict the appropriate coordination isomer for four out of five cases, while hybrid functionals (B3PW91, B3LYP) and PM3(tm) correctly predicted three out of five complexes (table 1).

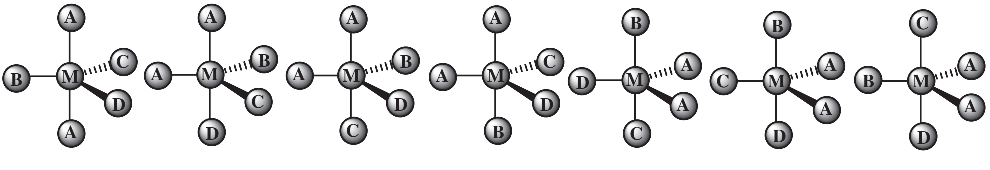
All five complexes in the MA_2B_2C class (scheme 5) have a singlet ground state as predicted by PM3(tm) calculations. For the complexes FALTAN [49] [$CoI_2(NO)(PMe_3)_2$], FAWHAM [50] [$Ir(CO)_2(CO_2Me)(PPh_3)_2$] (phosphine ligands in *ax–ax* position), QUGCIE [51] [$TaCl_2(CH_2Ph)$(2,3,5,6-tetraphenylphenoxy)$_2$] (2,3,5,6-tetraphenylphenoxy in *ax–ax* positions), and TOJMAG [52] [$W(NPh)(CH_2SiMe_3)_2(OC(CF_3)_3)_2$] (NPh and $OC(CF_3)_3$ situated in *ax* positions), all computational predictions are in agreement with experimental results. For the last member of this class MAJFEI [53] [$Co(CO)_2I(PEt_3)_2$], BPW91 and PM3(tm) reproduced the experimental geometry, with both phosphine ligands situated in *ax* positions, while a different coordination isomer with both phosphines situated in *eq* and iodine in an *ax* coordination site was predicted to be more stable) by B3PW91 ($\Delta E_{\text{calc–expt}} = 0.90$ kcal/mol), B3LYP (0.94 kcal/mol), MP2//HF (1.45 kcal/mol) and BLYP, where the energy difference is insignificant (0.01 kcal/mol).

PM3(tm), together with BPW91, accurately reproduces the crystallographic coordination isomer for all five species from the MA_2B_2C class, outperforming more sophisticated DFT functionals (B3PW91, B3LYP, BLYP) and MP2//HF, all of which yield four out of five accurate predictions (table 1).

All four complexes from the MA_2BCD class (scheme 6) were predicted by PM3(tm) calculations to have a singlet spin state. The results of all computational methods have



Scheme 5. MA_2B_2C.



Scheme 6. MA_2BCD.

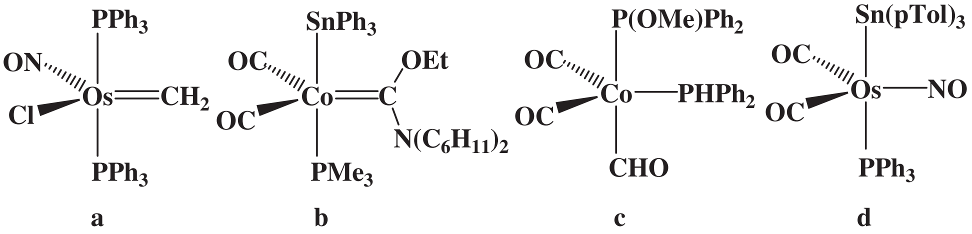


Figure 1. Lowest energy conformation isomers for MA_2BCD species.

reproduced the experimentally observed coordination isomers for CAMTEP [54] $[Os(CH_2)Cl(NO)(PPh_3)_2]$, with both phosphines situated in the *ax* position (figure 1a), GIPYAF [55] $[Co(CO)_2(SnPh_3)(PMe_3)(=C(OEt)(N(C_6H_{11})_2)]$ with $SnPh_3$ and PMe_3 in *ax* positions (figure 1b), and VEBDEM [56] $[Co(CO)_2(COMe)(PHPh_2)\ (POMePh_2)]$, with COMe and $P(OMe)Ph_2$ situated in *ax* sites (figure 1c). For RUTKAS [57] $[Os(CO)_2(NO)(PPh_3)(Sn(pTol)_3)]$, PPh_3 and $Sn(pTol)_3$ are positioned in *ax* sites (figure 1d). All theoretical methods reproduced the experimental geometry of RUTKAS, except PM3(tm), where CO and $Sn(pTol)_3$ were predicted to be situated in *ax* coordination sites. This coordination isomer is calculated to be more stable than the crystallographic isomer (figure 1d) by 6.12 kcal/mol.

All theoretical methods accurately predicted the correct coordination isomer for all four investigated species in the MA_2BCD class, except PM3(tm), where three out of four were predicted accurately (table 1).

3.3. *ONIOM calculations*

Overall, the PM3(tm) semiempirical Hamiltonian predicts the correct coordination isomer in 80% of the cases (table 1), while *ab initio* and DFT methods are correct approximately 90% of the time. This suggests that in most cases electronic factors are most significant in determining the correct coordination isomer. For some species, however, the steric effects created by truncating the ligands seem to be more important than electronic factors. In these particular cases, to clarify whether changing the steric effect of the ligands led to erroneous predictions, more calculations were performed on full models for each species. For this purpose all species where one or more DFT methods failed to reproduce crystallographic data were selected: CAJZOC [33], DTHFEC [34], CAFKOJ [46], RASQUX [48] and MAJFEI [53]. For two different TBP5 classes (MA_3B_2 and MA_2BCD) DFT methods reproduce the experimental coordination isomer for all species studied. To extend the calculations to all five TBP5 classes, additional calculations were chosen for species where either MP2//HF or PM3(tm) failed to provide an appropriate coordination isomer (CPETCP [42] and RUTKAS [57], respectively). In total, 27 distinct coordination isomers can be generated for these seven complexes.

To perform DFT calculations for full models is, in many cases, not feasible in the context of a very rapid *de novo* structural prediction scheme for transition metal complexes, especially when taking into consideration the size of the structures and the numbers of possible geometric, conformational, structural and coordination isomers. An alternative is provided by ONIOM [58] methods, where the molecular structure is divided into two different ‘layers’, each of which is treated at a different level of theory.

However, there are still 27 coordination isomers to be studied (each with many possible conformational isomers), and hybrid quantum mechanics/molecular mechanics (QM/MM) calculations are still much more time-consuming than SEQM techniques. The number of conformational isomers to be considered was reduced using a *de novo* pyramid algorithm constructed from a succession of different levels of theory [15].

Initially, each of the 27 coordination isomers (representing seven distinct stoichiometries) was built from scratch. An MM-based conformational search and geometry optimizations were performed using the MMFF94 [59] force field available in Spartan'04 [26]. After conformer searching, approximately 100 unique structures were obtained, which were optimized with the PM3(tm) method. The lowest energy unique coordination isomers resulting from the PM3(tm) optimizations were then optimized using the ONIOM QM/MM method and compared to experiment.

The QM/MM methods used in this research consisted of two levels of theory: the higher level used for describing the metal and its ligating atoms, entitled the B3LYP functional and CEP-31G basis set, with polarization functions for 'p' block elements; all other atoms were modeled with the universal force field (UFF) [60]. For all seven species ONIOM methods accurately reproduced the experimentally determined data.

4. Summary and conclusions

The goal of this research was to investigate the ability to predict the ground state coordination isomers for TBP5 transition metal complexes through the use of very rapid semiempirical quantum mechanics, and to compare SEQM techniques with much more expensive *ab initio* and DFT methods. All calculations performed at the different levels of theory used identical initial geometry guesses for all possible coordination isomers (111), corresponding to 30 distinct complexes and five different classes of TBP5 complexes. The results draw attention to pure DFT functionals, which replicated crystallographic data for 27 out of 30 species (90%), while hybrid functionals DFT and MP2//HF reproduced the coordination isomers for 26 out of 30 complexes (87%). Respectably close to these results – 24 out of 30 species, or 80% – were the predictions provided by much less expensive PM3(tm) parameterization methods (typical geometry optimization and frequency calculations took less than 10 minutes, as compared with *ab initio* and DFT methods, where geometry optimizations and frequency calculations ranged from 5 hours to 10 days). For those species where quantum methods on truncated models failed to reproduce crystallographic data, a *de novo* protocol, defined in this case by successive levels of theory succession, MM → PM3(tm) → ONIOM, applied to the full complex accurately reproduced the experimental data. The present results suggest that (a) electronic factors dominate steric effects in the determination of the correct ground state coordination isomer, and (b) semiempirical methods can play an important role in an integrated *de novo* structural prediction scheme for transition metal complexes.

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