

## Can Semiempirical Quantum Mechanics Be Used To Predict the Spin State of Transition Metal Complexes? An Application of *De Novo* Prediction

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### Introduction

Computational design of metal-containing complexes that have targeted functions has become an attainable goal since computer power has increased and computational chemistry codes have become more sophisticated. *De novo* structural prediction is a pyramid approach that employs a variety of different computational methods to generate the complete structure of a metal-containing complex. The base of the *de novo* design pyramid is a computationally inexpensive technique such as molecular mechanics (MM). Molecular mechanics is a good predictor of steric interactions, so that any structures with high MM energies can be eliminated. Candidates that survive the MM screen are submitted to semiempirical quantum mechanics (SEQM), which requires significantly fewer parameters than MM. However, SEQM methods take much longer per geometry optimization step than MM methods, so for the best efficiency, the SEQM step should be focused on the smallest number of structures feasible. Structures with high SEQM energies are also eliminated, resulting in a small set of targets that can be submitted to the computationally expensive *ab initio* methods. Finally, *ab initio* quantum mechanical (QM) methods are used on the best candidates to obtain accurate energies and structures. Each elimination step in *de novo* structural prediction requires the MM or SEQM method to *reliably* reject high-energy structures.

Part of the challenge in modeling transition metal-containing complexes is the chemical diversity of the metals. In particular, *de novo* structural prediction recognizes that there are many levels of isomerization for coordination complexes: (i) geometric isomers (e.g., *mer* versus *fac* for octahedral complexes), (ii) structural isomers (e.g., tetrahedral versus square planar for four-coordinate complexes), (iii) coordination isomers (e.g., *axial* versus *equatorial* for trigonal bipyramidal complexes), (iv) linkage isomers (e.g., cyanide

versus isocyanide), and (v) spin “isomers” (typically for open shell  $d^{3-7}$  metal ions).

A separate paper on *de novo* structural prediction has dealt with item (i).<sup>1</sup> It was found that MM-based conformational searching followed by SEQM geometry refinement accurately predicts the correct ground-state geometric isomer (*cis* versus *trans*, *fac* versus *mer*, and more complicated cases of geometric isomerism) for technetium (Tc) complexes.<sup>1</sup> In this Note, we focus on the reliable computational prediction of spin state. Complexes of Tc are chosen because of their importance in radioimaging<sup>2</sup> and nuclear waste remediation<sup>3</sup> and because they are found in a diverse variety of chemical environments. Thus, Tc complexes offer a rigorous computational test because their rich diversity is difficult to model *a priori*. Spin state-dependent properties of first-row transition metal complexes have been extensively studied but were not chosen for study because previous work casts doubt on the accuracy of PM3(tm) for many of these metals.<sup>4</sup>

### Computational Methods

A semiempirical quantum mechanics (SEQM) parametrization within the PM3(tm) Hamiltonian was genetics algorithm (GA) optimized for prediction of geometries.<sup>5</sup> The parametrization process

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**Table 1.** Relative Spin State DFT Energies (in kcal/mol) for Four Different Functionals

Refcode <sup>a</sup>	$E_{is-ls}^b$				$E_{hs-ls}^c$			
	B3LYP	BLYP	BP86	B3P86	B3LYP	BLYP	BP86	B3P86
BAJDQF	-17	-14	-14	-17	63	69	69	63
FOPBER <sup>e</sup>	17	21	21	18				
JEVMAV	-20	-15	-16	-28	32 <sup>d</sup>	33	32	23 <sup>d</sup>
JOWCON	68	63	102	69	136 <sup>d</sup>	135	161	146
KOMNEF	-20	-17	-17	-20	42	47	47	41
KUWSAW	13	15	14	13	84	83	79	83
LALGUA <sup>f</sup>	-22	-17	-17	-22				
KIMXIN	42	49	50	42	87	100	101	88
VICLIC	-7	-3	-3	-7	18	26	26	17
VIXRAV	-4	1	1	-4	25	33	33	24
WACXIH	72	75	75	72	134	141	141	134

<sup>a</sup> The refcode is the CSD<sup>7</sup> designation for the complex. A complete list of chemical formulas and original literature references is found in ref 11–13. <sup>b</sup>  $E_{is-ls}$  is the relative energy in kcal/mol of intermediate spin state versus the low spin state. <sup>c</sup>  $E_{hs-ls}$  is the relative energy in kcal/mol of high spin state versus the low spin state. <sup>d</sup> These complexes did not converge using a restricted calculation, so the unrestricted BP86/CSDZ\* formulation was employed to calculate this high spin state. No appreciable spin contamination was observed as revealed by the calculated expectation values of  $S^2$ . <sup>e</sup> FOPBER,  $[\text{Tc}(o\text{-C}_6\text{H}_4\text{S}_2)_3]^-$ , is a formally  $d^2\text{-Tc(V)}$  complex, and thus, a high spin, quintet state was not calculated. <sup>f</sup> LALGUA,  $\text{trans-TcCl}_4(\text{PMe}_3)_2$ , is a formally  $d^3\text{-Tc(IV)}$  complex, and thus, a high spin, sextet state was not calculated.

has been described more fully in a previous contribution.<sup>5</sup> PM3-GA for Tc can on average predict experimentally measured Tc-dependent bond lengths, bond angles, and dihedral angles to within 0.06 Å, 2°, and 4°, respectively,<sup>5</sup> a level of accuracy commensurate with higher-level, *ab initio* calculations.<sup>6</sup>

The solid-state structures of all the target species are available in the Cambridge Structural Database (CSD).<sup>7</sup> Structures were extracted from the CSD and imported into HyperChem,<sup>8</sup> and hydrogen atoms added at fixed, normal single bond distances. A variety of paramagnetic and diamagnetic complexes were chosen to test the performance of PM3-GA. In all cases, the geometries from the CSD were used without any structural modification other than the addition of the hydrogens.

This research employed the HyperChem<sup>8</sup> and Jaguar<sup>9</sup> packages.

## Results and Discussion

One important goal in *de novo* structure prediction is to use the least expensive computational tool to screen structures and reliably eliminate high-energy candidates. Because spin states are determined by the electronic configuration of the metal ion, MM cannot be used for spin state prediction. The question is whether SEQM methods are sufficiently accurate to predict the spin state of transition metal complexes. If not, then more expensive *ab initio* methods will be required. Given the paucity of reported spin states in the literature, and because most of the complexes from the CSD have unknown experimental spin states, we assume that DFT computations with the BP86 functional and CSDZ\* basis set<sup>10</sup> will correctly predict the multiplicity of the ground-state configuration.

(8) *Hyperchem*, version 6.02; HyperCube, Inc.: Gainesville, FL, 2000; <http://www.hyper.com>.

(9) *Jaguar*, version 4.0; Schrodinger, Inc.: Portland, OR, 2000; <http://www.schrodinger.com/Products/jaguar.html>.

(10) The CSDZ\* basis set employs Stevens' ECP and VBS for heavy elements (augmented by a  $d$  polarization function for heavy main group elements) and the 6-31G\* basis set for hydrogen and the light main group elements. Stevens, W. J.; Krauss, M.; Basch, P.; Jasien, P. G. *Can. J. Chem.* **1992**, *11*, 55.

Searching the CSD for high quality ( $R < 10\%$ ), monomeric, neutral Tc complexes with no reported crystallographic disorder and no reported errors yielded roughly 200 structures. Of these, 50 complexes of a size amenable to DFT computation ( $<1000$  basis functions) were selected.<sup>11–13</sup> These 50 structures represent a variety of oxidation states (11 are Tc<sup>I</sup>; 8 are Tc<sup>II</sup>; 25 are Tc<sup>III</sup>; 6 are Tc<sup>V</sup>), coordination numbers (10 are five-coordinate; 33 are six-coordinate; 7 are seven-coordinate), and ligand types (thiolate, oxo, phosphine, arsine, amine, imine, enolate, amide, carboxylate, thiocarboxylate, CO, NO, nitrile, *S*-sulfoxide, NS, phosphine oxide, pentamethylcyclopentadienyl, tris(pyrazolyl)borate, imido, cyclopentadienyl, *S*-thiocyanate, and dithiophosphate). There was no *a priori* knowledge of the spin state of any of the 50 complexes.

Four levels of SEQM (using HyperChem<sup>8</sup>) and two *ab initio* levels (using Jaguar<sup>9</sup>) were utilized for single point energy calculations on the 50 Tc complexes: (i) extended Hückel theory (EHT), (ii) restricted ZINDO/1 (rZINDO), (iii) unrestricted ZINDO/1 (uZINDO), (iv) restricted PM3 (rPM3), (v) unrestricted PM3 (uPM3), (vi) restricted open-shell Hartree–Fock (ROHF), and (vii) DFT computations. For even-electron systems, 43 of the 50 complexes, single point

- (11) (a) BECEDS, carbonyl-tris(diethylthiocarbamato)-technetium(II): Baldas, J.; Bonnyman, J.; Pojer, P. M.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1982**, 451. (b) CETBEI, tris(diethylthiocarbamato)-dimethylphenylphosphine-technetium(III): Bat-sanov, A. S.; Struchkov, Y. T.; Lorenz, B.; Wahren, M. Z. *Inorg. Allg. Chem.* **1984**, *510*, 117. (c) CMPPTC, carbonyl-trichloro-tris(dimethylphenylphosphine)-technetium: Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1978**, 373. (d) DOFLEP, *trans*-dicarbonyl-bis(dimethylphenylphosphine)-(N,N'-diphenyl-acetamidinato-N,N')-technetium(I): Marchi, A.; Rossi, R.; Duatti, A.; Magon, L.; Bertolasi, V.; Ferretti, V.; Gilli, G. *Inorg. Chem.* **1985**, *24*, 4744. (e) DUCRAU, dibromo-tris(*tert*-butyl-isocyanide)-nitrosyl-technetium(I): Linder, K. E.; Davison, A.; Dewan, J. C.; Costello, C. E.; Maleknia, S. *Inorg. Chem.* **1986**, *25*, 2085. (f) FEVSAA, chloro-dimethylphenylphosphine-bis(N-phenylsalicylideneiminato-N,O)-technetium(III): Duatti, A.; Marchi, A.; Luna, S. A.; Bandoli, G.; Mazzi, U.; Tisato, F. *J. Chem. Soc., Dalton Trans.* **1987**, 867. (g) FOLJUL, tris(monothiodibenzoylmethanato-O,S)-technetium(III): Bandoli, G.; Mazzi, U.; Spies, H.; Munze, R.; Ludwig, E.; Uhlmann, E.; Scheller, D. *Inorg. Chim. Acta* **1987**, *132*, 177. (h) GAYNAV, bis(acetonitrile-N)-tris(2,3,5,6-tetramethylbenzenethiolato)-technetium(III): de Vries, N.; Dewan, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574. (i) GAYNEZ, (acetonitrile-N)-carbonyl-tris(2,3,5,6-tetramethylbenzenethiolato)-technetium(III): de Vries, N.; Dewan, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574. (j) GAYNID, carbonylpyridyl-tris(2,3,5,6-tetramethylbenzenethiolato)-technetium(III): de Vries, N.; Dewan, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574. (k) GEMNER, (*S*-(1-morpholinyl)ethyl)-(N,N'-ethylenebis(2-mercaptoacetamide)-N,N',S,S')-technetium(V): Bryson, N.; Dewan, J. C.; Lister-James, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 2154. (l) GIZGUR, (picolineamine-N-acetato-N-acetic acid)-tricarbonyl-technetium: Alberto, R.; Schibli, R.; Egli, A.; Schubiger, A. P. *J. Am. Chem. Soc.* **1998**, *120*, 7987. (m) GOFZAC, dichloro-nitrosyl-triphenylphosphine-(2-pyridyldiazenido)-technetium(I): Nicholson, T.; Hirsch-Kuchma, M.; Freiberg, E.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1998**, *279*, 206. (n) GOGQIC, acetonitrilo-tris(2-mercapto-methyltetrazolato)-triphenylphosphine-technetium: Abram, U.; Dilworth, J. R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 609. (o) HEGDEC, *cis*-(4-chlorophenyldiazenido)-(N,N'-bis(salicylidene)ethane-1,2-diamino)-triphenylphosphino-technetium: Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; Povey, D. C.; Archer, C. M.; Kelly, J. D. *J. Chem. Soc., Dalton Trans.* **1994**, 1251. (p) JABJAX, *trans*-dichloro-bis(1,2-bis(diphenyl)phosphinoethane-P,P')-technetium(II): Libson, K.; Doyle, M. N.; Thomas, R. W.; Nelesnik, T.; Woods, M.; Sullivan, J. C.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3614. (q) JATZAF, *cis*-dichloro-*trans*-bis(dimethylphenylphosphine)-(1,10-phenanthroline-N,N')-technetium(II): Wilcox, B. E.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 3917.

## NOTE

energies were computed for singlet (low spin), triplet (intermediate spin), and quintet (high spin) states. For the remaining 7 odd-electron systems, single point energies were computed for doublet (low spin), quartet (intermediate spin), and sextet (high spin) states.

To evaluate the effect of functional on spin state prediction, single point energies were computed for 11 complexes with hybrid (B3LYP and B3P86) and pure DFT (BLYP and BP86), gradient-corrected functionals (Table 1). In all cases, a restricted open-shell DFT formulation was used to obviate the problem of spin contamination.<sup>14</sup> From Table 1, we conclude that there is little difference among the functionals with respect to relative energies of the spin states. Because many of the complexes in this study do not have experimentally determined spin states, we chose the BP86 functional (restricted open-shell formulation) as the benchmark because of its superior convergence behavior as compared to the B3 functionals.

As anticipated, the EHT calculations all predicted the low spin state to be the most stable, which does not agree with the DFT computations. The BP86/CSDZ\* computations predict a low spin ground state for all Tc complexes, except FEVSAA,<sup>11f</sup> FOLJUL,<sup>11g</sup> JEGYOJ,<sup>12d</sup> KABMIJ,<sup>12g</sup>

KIPMOL,<sup>12j</sup> VICLIC,<sup>13j</sup> YASLEJ,<sup>13m</sup> ZEMZOG,<sup>13o</sup> and ZOZLOP.<sup>13p</sup> All of these except VICLIC are pseudo-octahedral d<sup>4</sup>-Tc<sup>III</sup> complexes for which available experimental evidence suggests a triplet ground state, which is expected for a (t<sub>2g</sub>)<sup>4</sup> electronic configuration, and which is also consistent with the DFT computations. There are three six-coordinate, d<sup>4</sup>-Tc<sup>III</sup> complexes predicted by DFT to have singlet ground states, i.e., HEGDEC<sup>11o</sup> ( $E_s < E_t$  by 41 kcal/mol), KUWSAW<sup>12m</sup> ( $E_s < E_t$  by 14 kcal/mol), and VEFGAO<sup>13i</sup> ( $E_s < E_t$  by 23 kcal/mol). HEGDEC is a hydrazido complex formulated as an 18-electron species and thus expected to be diamagnetic, consistent with the lack of upfield <sup>1</sup>H NMR shifts seen for other paramagnetic Tc<sup>III</sup> complexes and both DFT and SEQM predictions. No definitive assignment of the ground spin state of VEFGAO is reported. KUWSAW is determined to be a triplet ground state by the Evans NMR method.<sup>12m</sup>

KUWSAW, [tris(diphenyl(*o*-phenylthiolato)phosphine)Tc], and VICLIC, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TcCl], presented obvious problems for DFT calculations, which consistently predicted the singlet and triplet as the ground state, respectively, for all functionals studied (Table 1). Because VICLIC is an 18-electron

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- (14) A series of computations using the unrestricted Kohn-Sham formalism were carried out at the BP86/CSDZ\* level of theory. No substantial differences in spin state energies were observed vis-à-vis the restricted open-shell BP86/CSDZ\* computations.

**Table 2.** Calculated Spin State Energy Differences (kcal/mol)

Refcode <sup>a</sup>	CN	d <sup>*n</sup>	DFT		ROHF		uPM3		rPM3		rZINDO		uZINDO	
			is-ls	hs-ls	is-ls	hs-ls	is-ls	hs-ls	is-ls	hs-ls	is-ls	hs-ls	is-ls	hs-ls
GEMNER	5	d <sup>2</sup>	47	d <sup>2e</sup>	32	d <sup>2e</sup>	72	d <sup>2e</sup>	76	d <sup>2e</sup>	72	d <sup>2e</sup>	29	d <sup>2e</sup>
SOJSEP	5	d <sup>2</sup>	50	d <sup>2e</sup>	78	d <sup>2e</sup>	46	d <sup>2e</sup>	57	d <sup>2e</sup>	96	d <sup>2e</sup>	92	d <sup>2e</sup>
GAYNAV	5	d <sup>4</sup>	42	84	22	35	45	89	62	122	34	66	18	34
GAYNEZ	5	d <sup>4</sup>	50	103	54	86	52	114	67	152	48	88	27	54
GAYNID	5	d <sup>4</sup>	48	100	54	86	46	168	65	dnc <sup>c</sup>	47	92	28	56
GOGQIC	5	d <sup>4</sup>	43	84	68	35	59	111	64	148	31	56	15	26
JAVZEL	5	d <sup>4</sup>	45	89	27	104	87	98	60	114	33	110	17	33
JAWDAM	5	d <sup>4</sup>	54	120	57	94	90	128	74	144	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>
JEGDOO	5	d <sup>4</sup>	47	98	36	94	50	92	56	106	54	103	12	42
LEWXAM10	5	d <sup>4</sup>	50	94	29	49	66	106	63	125	33	106	19	33
PCLTCA10	6	d <sup>2</sup>	30	d <sup>2e</sup>	-3	d <sup>2e</sup>	38	d <sup>2e</sup>	63	d <sup>2e</sup>	60	d <sup>2e</sup>	19	d <sup>2e</sup>
SOSMOC	6	d <sup>2</sup>	20	d <sup>2e</sup>	38	d <sup>2e</sup>	12	d <sup>2e</sup>	38	d <sup>2e</sup>	42	d <sup>2e</sup>	18	d <sup>2e</sup>
TOQCOR	6	d <sup>2</sup>	29	d <sup>2e</sup>	34	d <sup>2e</sup>	100	d <sup>2e</sup>	49	d <sup>2e</sup>	51	d <sup>2e</sup>	14	d <sup>2e</sup>
YUBGAD	6	d <sup>2</sup>	23	d <sup>2e</sup>	35	d <sup>2e</sup>	51	d <sup>2e</sup>	46	d <sup>2e</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>
FEVSAA	6	d <sup>4</sup>	-15	25	-38	35	-22	-13	-18	24	-4	97	-25	65
FOLJUL	6	d <sup>4</sup>	-10	24	-34	11	-26	33	0	27	-3	dnc <sup>c</sup>	-23	43
HEGDEC	6	d <sup>4</sup>	41	92	21	56	30	51	47	99	42	113	18	90
JEGYOJ	6	d <sup>4</sup>	-18	14	-40	7	-33	-26	-6	16	-7	97	-24	62
KABMIJ	6	d <sup>4</sup>	-23	25	-43	-13	-22	-22	-9	34	-9	100	-25	79
KIPMOL	6	d <sup>4</sup>	-17	46	-36	69	-23	-5	-4	67	-9	67	-27	28
KUWSAW	6	d <sup>4</sup>	14	79	-3	91	dnc <sup>c</sup>	dnc <sup>c</sup>	24	104	14	86	-9	38
VEFGAO10	6	d <sup>4</sup>	23	96	7	100	18	65	36	101	21	108	1	68
YASLEJ	6	d <sup>4</sup>	-20	46	-35	58	-25	-13	-11	27	-10	84	-25	76
ZEMZOG	6	d <sup>4</sup>	-20	41	-36	8	-15	-26	-13	26	-11	86	-27	18
ZOZLOP	6	d <sup>4</sup>	-14	44	-36	10	-22	44	-4	62	-6	84	-25	21
JABJAX <sup>d</sup>	6	d <sup>5</sup>	48	113	50	71	dnc <sup>c</sup>	dnc <sup>c</sup>	54	117	45	105	34	73
JATZAF <sup>d</sup>	6	d <sup>5</sup>	34	87	26	103	3	27	26	76	61	116	63	74
JOWCON <sup>d</sup>	6	d <sup>5</sup>	102	161	-33	-75	7	-8	41	98	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>
KIMXIN <sup>d</sup>	6	d <sup>5</sup>	50	101	-17	-5	59	121	30	69	40	115	35	82
RIMMEF <sup>d</sup>	6	d <sup>5</sup>	46	99	18	6	26	88	26	69	25	125	31	78
VAPSOU <sup>d</sup>	6	d <sup>5</sup>	67	148	127	110	31	34	67	139	2	63	18	66
VAPSUA <sup>d</sup>	6	d <sup>5</sup>	63	151	77	114	0	41	dnc <sup>c</sup>	dnc <sup>c</sup>	22	90	23	175
DOFLEP	6	d <sup>6</sup>	62	144	97	189	35	103	55	138	56	133	38	103
DUCRAU	6	d <sup>6</sup>	47	114	27	65	37	193	50	122	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>
GIZGUR	6	d <sup>6</sup>	62	146	70	163	39	102	48	121	80	184	85	148
GOFZAC	6	d <sup>6</sup>	31	102	18	33	13	81	26	79	55	128	14	46
JOWKIP	6	d <sup>6</sup>	75	165	96	190	55	159	75	152	48	141	37	113
KESDOB	6	d <sup>6</sup>	65	136	90	183	dnc <sup>c</sup>	89	42	106	45	136	35	97
KITDAS	6	d <sup>6</sup>	89	173	91	183	60	109	75	134	84	208	104	180
LAKROE	6	d <sup>6</sup>	85	168	93	182	59	138	85	155	108	221	92	209
NUSVEC	6	d <sup>6</sup>	74	155	85	187	65	111	46	91	81	188	68	150
POSLUE10	6	d <sup>6</sup>	86	172	90	176	78	135	81	171	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>
SOHBEW	6	d <sup>6</sup>	52	107	13	32	30	111	48	95	31	125	16	54
BECDDES	7	d <sup>4</sup>	47	97	33	65	33	62	50	103	61	150	39	83
CETBEI	7	d <sup>4</sup>	36	74	18	34	21	37	42	82	35	71	22	46
CMPPTC	7	d <sup>4</sup>	62	121	77	174	91	86	54	107	77	130	53	100
KIZYEK	7	d <sup>4</sup>	50	106	46	41	40	72	45	84	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>	np <sup>b</sup>
SICBIP	7	d <sup>4</sup>	48	103	54	93	44	96	58	110	93	160	65	92
VICLIC	7	d <sup>4</sup>	-3	26	-23	-23	82	12	33	90	23	147	8	46
VIXRAV	7	d <sup>4</sup>	1	33	9	-20	29	70	52	117	81	136	73	156

<sup>a</sup> The Refcode is the Cambridge Structural Database<sup>7</sup> designation for the complex. A complete list of chemical formulas and original literature citations is found in ref 11–13. CN is the coordination number of the technetium; d<sup>\*n</sup> is the d-electron configuration of the technetium as deduced by its formal oxidation state. The quantities is-ls and hs-ls are the calculated energies (kcal/mol) for the intermediate (triplet and quartet for even- and odd-electron species, respectively) and high (quintet and sextet for even- and odd-electron species, respectively) spin states in relation to the low spin (singlet and doublet for even- and odd-electron species, respectively) state. <sup>b</sup> The complex contains atoms (Br and/or As) for which ZINDO/1 is not parametrized. <sup>c</sup> The complex did not converge in a particular spin state for the BP86/CSDZ\* level of theory despite repeated attempts with different initial guesses obtained with different functionals and basis sets. <sup>d</sup> Odd-electron species. <sup>e</sup> This complex is a d<sup>2</sup>-Tc<sup>V</sup> species, and hence, a quintet (high spin in our notation) state was not studied.

organometallic complex, it seems unlikely that the complex is paramagnetic. The original literature reports that the complex is diamagnetic.<sup>13j</sup> All SEQM methods predicted a singlet ground state for VICLIC, so we assume the DFT calculations are in error and that the correct spin state is indeed the singlet. In addition, BP86/CSDZ\* predicts a singlet more stable than the triplet by 14 kcal/mol for KUWSAW.<sup>12m</sup> However, the experimental literature reports

a magnetic susceptibility,  $\mu = 3.0 \mu_B$ , for the complex, indicating a triplet.<sup>12m</sup> The causes of these errors by DFT are not apparent.

Interestingly, the ROHF/CSDZ\* computations predict a different ground spin state than DFT for six of the 50 complexes (JOWCON, KIMXIN, KUWSAW, PCLTCA10, VICLIC, and VIXRAV;<sup>11–13</sup>). ROHF shows the sextet (high spin) state as more stable than the quartet by 42 kcal/mol

## NOTE

for JOWCON, the quartet is more stable than the doublet by 17 kcal/mol for KIMXIN, and the triplets are more stable than the singlets by 3 kcal/mol each for KUWSAW and PCLTCA10. BP86/CSDZ\* predicts lowest spin states as the ground state by 102 kcal/mol for JOWCON, 50 kcal/mol for KIMXIN, and 30 kcal/mol for PCLTCA10. ROHF/CSDZ\* predicts the same triplet ground state for KUWSAW as noted in the experimental literature.<sup>12m</sup> KIMXIN is determined to be a doublet by ESR,<sup>12i</sup> a result consistent with the DFT and SEQM (*vide infra*) predictions, Table 2, but not the quartet predicted by ROHF. The spin states for JOWCON<sup>12e</sup> and PCLTCA10<sup>12q</sup> are not discussed in the experimental papers, but the latter is a Tc<sup>V</sup>-oxo complex, which is most likely a singlet as predicted by every other method other than ROHF/CSDZ\*. JOWCON is a d<sup>5</sup>-Tc<sup>II</sup> pseudo-octahedral complex, and thus, one would expect a doublet, (t<sub>2g</sub>)<sup>5</sup> electronic configuration. VIXRAV, [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)-Tc(η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>)], like VICLIC, is an 18-electron organometallic and thus expected to be a singlet as found by BP86/CSDZ\* and all SEQM methods, but not ROHF/CSDZ\*.

There are no ZINDO/1 parameters for Br and As in HyperChem, so DUCRAU, JAWDAM, JOWCON, KIZYEK, POSLUE10, and YUBGAD<sup>11-13</sup> were excluded from the ZINDO/1 analyses. rZINDO predicted the same ground state as DFT for 43 of the 44 complexes for which ZINDO/1 is fully parametrized. The only exception is VICLIC.<sup>13j</sup> rZINDO predicts a singlet ground state for VICLIC by 23 kcal/mol, which is in agreement with experiment but not with the BP86/CSDZ\* computations. Unrestricted ZINDO/1 calculations predicted the same spin state as DFT for all 44 complexes for which ZINDO/1 is fully parametrized (Table 2) with the exception of VICLIC and KUWSAW. Interestingly, uZINDO predicts a triplet state more stable than the singlet by 9 kcal/mol for KUWSAW, which is in agreement with the experimental literature.<sup>12m</sup> As noted before, the prediction of a singlet ground state by uZINDO for VICLIC is consistent with experimental measurements.<sup>13j</sup>

The restricted PM3 (rPM3) computations predicted the same spin state as DFT for all complexes except VICLIC. However, as noted previously, this is a case in which the BP86/CSDZ\* prediction does seem to be in disagreement with the experimental evidence.<sup>13j</sup> For uPM3, there are three points of disagreement with BP86/CSDZ\*-predicted spin states other than VICLIC: JOWCON,<sup>12e</sup> KABMIJ,<sup>12g</sup> and ZEMZOG.<sup>13o</sup> For KABMIJ, Tc(acac)<sub>3</sub>, a triplet spin state was indicated in the experimental paper, which is consistent

with all methods investigated here other than uPM3, for which the quintet state is calculated lower than the triplet, albeit by less than 1 kcal/mol. JOWCON<sup>12e</sup> is predicted to be a high-spin sextet by uPM3, and although the ground spin state is not discussed in the experimental papers as a d<sup>5</sup>-t<sub>2g</sub><sup>5</sup> pseudo-octahedral complex, would be expected to be a doublet as found by the DFT calculations. ZEMZOG is a d<sup>4</sup>-t<sub>2g</sub><sup>4</sup> pseudo-octahedral complex, which would lead one to predict a triplet ground state, not the quintet state predicted by uPM3. It is worth noting that PM3(tm) calculations showed more SCF convergence difficulties than ZINDO methods.

## Conclusions

We find that the SEQM methods ZINDO/1 and PM3 can reliably predict spin states as compared to DFT for Tc in a variety of different coordination environments, to the extent of out-performing much more expensive ROHF *ab initio* calculations. ZINDO demonstrated better SCF convergence behavior than PM3(tm) methods. However, the performance of the PM3(tm) methodology is still exemplary and has a slight advantage over ZINDO in terms of a larger array of parametrized atoms. Furthermore, our calculations suggest that the use of restricted open-shell SEQM wave functions is preferable to unrestricted wave functions. It is worth concluding by pointing out that a typical SEQM calculation took on the order of a few minutes on a personal computer, while the DFT computations required hours to days on an eight-processor SGI Origin2000. Hence, SEQM methods comprise a promising family of methods for reliable, very rapid *de novo* prediction of TM entities, for example, catalysts, metallodrugs, or novel nuclear waste complexants, and are worthy of further research to establish their reliability for other chemical properties and to develop improved parametrizations.

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