Molecular Mechanics Calculation of Titanium(IV) Schiff-Base Complexes

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The force field for Ti(IV) Schiff-base complexes having the general formula Ti(Schiff-base) Cl_2 (where Schiff-base = $^-OC_6H_4$–CH=N–$(CH_2)_n$–N=CH–$C_6H_4O^-$ and n = 2, 3, 4, 5, and 6) has been generated. Using the generated force-field minimum energy conformers have been predicted for the corresponding Ti(IV) complexes. It has been shown that when n = 2 and 3, the compound prefers a *trans*-configuration. In the case where n = 4, 5 and 6, the total energy difference between the *cis*- and *trans*-conformers are not large enough for one to make any definite predictions about the preferred conformation. However the total energy of the *trans*-conformer is also lower than that of the *cis*-conformer in these cases.

A description of the geometries of molecules based on a ball and spring has been in the literature for more than five decades.[1—3] Force fields developed by Allinger, such as MM1, MM2, and MM3, have been extensively used in modeling organic compounds.[4—7] However, molecular-mechanics calculations on inorganic and bioinorganic systems are limited by a number of factors.[8—12] There are no MM programs suitable for inorganic and bioinorganic force fields. The organic force field contains only few atoms, such as C, H, N, O, and S. The general force field for inorganic and bioinorganic systems should contain parameters for various oxidation and spin states in addition to the parameters for the organic ligand. The generation of force-field parameters from vibrational spectroscopy is also limited by the mixing of the ligand vibrational modes and various electronic effects. Although the partial charges around the metal ion are usually ignored in molecular-mechanics calculations, their influence in predicting the properties of large molecules and bioinorganic molecules has also been recognized.[13—18] Several inorganic and bioinorganic molecules adopt a large number of conformations, and computing their structure is computationally intensive and requires a number of approximations. The molecular-mechanics calculations on inorganic and bioinorganic molecules are also limited by the symmetry around the metal ion.[19—21]

Though there are certain difficulties in handling the molecular-mechanics calculations of inorganic and bioinorganic molecules, it has emerged as a useful tool in studying such molecules.[8—12] Molecular-mechanics calculations are widely used in assessing the steric arrangements of molecules and to gain insight into the nature of possible intramolecular and intermolecular interactions. Several applications of the molecular-mechanics method to transition-metal complexes have been reviewed by Brubaker and Johnson,[8] Comba,[9] and Hay.[10] Recently, the application of bioinorganic molecular mechanics calculations has also been reviewed by Zimmer.[11] Buckingham, Sargeson, and Snow have used molecular-mechanics calculations to predict the molecular geometries and stabilities of Co(III) (triethylenetetramine) [(S)-prolinato] complexes.[22] The structure, stereochemistries and stabilities of Co(III) (triethylenetetramine) (glycinate) complexes have been predicted using the molecular-mechanics approach.[23—25] A set of parametrized force field have been optimized for a series of Co(III),[26] Co(II),[27] Ni(II),[28,29] and Cu(II)[30] complexes. The applications of molecular mechanics to transition-metal complexes has included the computation of the three-dimensional structure, the isomer and conformer ratio, cavity size, metal-ion selectivity of ligands and estimation of the Franck–Condon barriers to electron-transfer relations and correlation kinetic and thermodynamic factors.[8—12,31] Comba and co-workers have used molecular mechanics to estimate the Jahn–Teller distortion in transition-metal complexes.[32] They have also generated force-field parameters for systems involving Cu(II), Ni(II), Co(III), Fe(III), Cr(III), Zn(II), and Rh(III) complexes with amine, carboxylato, pyridine and thioether ligands[33] as well as for some Ti(IV) and Co(IV) complexes.[34] The predicted bond lengths and bond angles are in good agreement with the observed X-ray structural data.[33,34]

We have recently synthesized a series of Ti(IV) complexes of composition $TiLCl_2$ (L = Schiff-bases of varying ring size) because of their possible applications in chemotherapy.[35] A titanium(IV) complex, budotitan [$Ti(bzac)_2(oet)_2$], (bzac = 1-phenylbutane-1,3-dionate, oet = ethoxide) has been proposed to be a promising drug, and is currently under clinical trial for chemotherapy.[36] Titanium(IV) complexes of the Schiff-base with ring size 12 (salen) has been shown to have a *trans*-dichloro arrangement based on its X-ray structure determination.[37] On the other hand, when the ring size is longer, there is always a possibility of ring folding around to

give a *cis*-structure. Our spectroscopic studies, however, show that in all of these complexes where the ring size varies from 12 to 16 the complex prefers a *trans*-dichloro configuration.[35] In this communication we describe our effort to calculate and predict the preferred conformation for the Ti(IV) complexes with Schiff-base ligands having a ring size varying from 12 to 16.

Although the application of the molecular-mechanics approach to transition-metal complexes and many-bodied systems including metalloprotein are enlarging, some special constraints are encountered in employing several standard force-field calculations packages. A high symmetry of a coordination shell containing more than two ligand donor atoms of the same type poses an additional constraint which is not faced in the case of many organic compounds. It arises from the need for labeling identical donor atoms differently, and thus a multiple referencing problem has been a serious constraint to a more full exploitation of the molecular-mechanics approach. In this investigation we have been able to label a set of chemically equivalent nitrogen, oxygen and chlorine atoms differently in a related series of titanium(IV) complexes of Schiff-base ligands through suitable modifications to the MM2 source data.

A set of optimized force fields for a homologous series of Schiff-base complexes of Ti(IV) [where Schiff-base = $^{-}OC_6H_4$–CH=N–$(CH_2)_n$–N=CH–$C_6H_4O^{-}$ and $n = 2$ (salen), 3 (salprn), 4 (salbuen), 5 (salpent), and 6 (salhex)] has been presented. The total strain energies have been computed for both *cis*- and *trans*-arrangements of tetradentate ligands. Based on the force-field calculations some structural generalizations on Ti(IV) Schiff-base complexes have been possible.

Computational Details

The force-field package MM2, developed by Allinger and Yuh,[38] and later modified by Perkovic and Endicott,[39] for application to transition metal complexes was employed. A multiple-referencing problem associated with the molecules, Ti(Schiff-base)Cl_2 originates from the need to define a set of chemically equivalent nitrogen, oxygen and chlorine atoms differently. The multiple-referencing problem was overcome in this study for an analysis of a homologous series of complexes by numbering chemically equivalent sets of nitrogen, oxygen and chloride atoms differently.[40] In the modified package, the type number 8 and 26 have been taken to define imine nitrogen and types 6 and 7 have been used as O. The respective parameters in the original data base have been changed according to the new definition of atoms. All other parameters related to Ti–N, Ti–O, O–Ti–O, N–Ti–N, and O–Ti–N are externally given in the input prepared for the calculation.

Within the molecular-mechanics framework the structure of a molecule is modified in order to minimize its total strain energy consisting of the bond-length deformation (E_b), bond-angle deformation (E_θ), nonbonded interaction (E_{nb}), torsional deformation (E_ω), and electrostatic interaction (E_{es}). The potential function used in the calculation is given by

$$E_{Total} = E_b + E_\theta + E_\omega + E_{nb} + E_{es}, \quad (1)$$

Here,
$$E_b = 1/2k_r(r_{ij} - r_0)^2, \quad (2)$$

where k_r is the stretching force constant, r_{ij} the bond length, and r_0 the strain free bond length;

$$E_\theta = 1/2k_\theta(\theta_{ijk} - \theta_0)^2, \quad (3)$$

where k_θ is the angle bending force constant, θ_{ijk} is the bond angle and θ_0 is the strain free bond angle;

$$E_\omega = V_1/2(1 + \cos\omega) + V_2/2(1 - \cos 2\omega) + V_3/2(1 + \cos 3\omega), \quad (4)$$

where V_1, V_2, and V_3 are the first-, second-, and third-order torsional constants. V_1 and V_3 destabilize the eclipsed form, while V_2 represents a minimum at 0° and 180°. ω is the torsional angle;

$$E_{nb} = -C/r^6 + A\exp(-Br), \quad (5)$$

where A, B, and C are estimated from the virial coefficients and van der Waals radii for similar gases and r is the nonbonded distance between the atoms considered for calculation

$$E_{es} = q_i \cdot q_j / 4\pi\varepsilon_0 r_{ij}, \quad (6)$$

where q_i and q_j are the charge on the atom and r_{ij} is the distance between two atoms having charge q_i and q_j and ε_0 is the permittivity of free space.

By varying the force field corresponding to the X-ray structural values, the force-field parameters for the Ti(salen)Cl_2 complexes have been optimized. The same potential functions have also been used to generate force-field parameters and to calculate the structural parameters for a series of bis(β-diketonato)titanium(IV) complexes. For these complexes, molecular-mechanics calculations have been performed by Comba and co-workers using MOMECPC, a strain energy minimization program for metal complexes.[34] The calculated geometrical parameters in this study are also in good agreement with the values obtained from previous work.[34] In each step, complete optimization was carried out on the geometry of Ti(salen)Cl_2. This approach has also been used by others in force-field calculations of transition metal complexes.[8,9,33]

Using a set of default values of standard values of bond lengths, the bond angles, and other geometrical parameters, initial atomic coordinates have been generated. The reference values for the bond lengths and bond angles have been chosen based on the geometry and minimum-energy arguments. The single-crystal X-ray structure of *trans*-Ti(salen)Cl_2 has already been reported.[37] By comparisons of the calculated and observed bond lengths and bond angles, the force field parameters employed in this study revalidated. By varying the force constants, the total strain energy has been calculated for Ti(salen)Cl_2 and the structural parameters optimized. A set of force constants have been chosen using a best-fit approach for calculating the structural parameters for the higher homologous of Ti(Schiff-base)Cl_2 complexes. Although no formal charge was assigned to the metal ion,

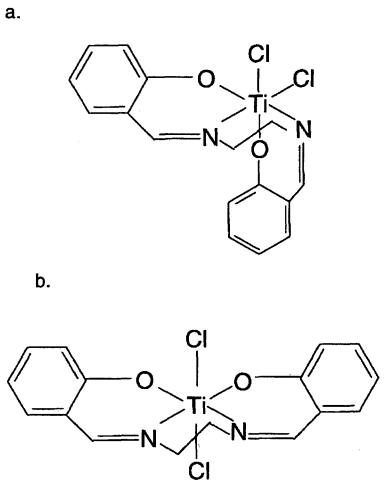

Fig. 1. Two conformations of Ti(IV) Schiff-base complexes. (a) *cis*- and (b) *trans*-.

the force constants of the metal–nitrogen and metal–oxygen were chosen in such a way to model Ti(Schiff-base)Cl_2 complexes. A van der Waals radius of 2.0 Å was used for Ti in the calculation. The nonbonded repulsive forces, bond-length deformation forces, bond-angle deformation forces, torsional forces, and nonbonded attractive forces are the major forces involved in the molecules which dominate other forces that arise in terms of their steric requirements. An understanding of the variation of these forces with respect to the increase in the CH_2 units in the complex is important. Therefore, an attempt was also made in this study to plot the various forces as a function of the number of CH_2 units. All torsional constants around the metal ion were taken to be zero. All calculations were performed on HP work station 9000—7000 series.

Results and Discussion

Force Field Parameters for Ti(IV) Complexes. Since only few relevant structures for Ti(IV) Schiff-base complexes are available, the development of force-field parameters for these complexes is difficult. We therefore used parameters for Cr(III) and Co(III) Schiff-base complexes for which well-established force field parameters are available.[8,41] The Ti-(IV) Schiff-base force field was developed on the basis of the reported structure of Ti(salen)Cl_2 and the force-field parameters reported by Comba and co-workers on a series of bis(β-diketonato)titanium(IV) complexes.

Table 1. Comparison of Selected Bond Lengths and Bond Angles of the X-Ray Structure of *trans*-Ti(salen)Cl_2 and Optimized Structures in the *cis*- and *trans*-Configuration

Bond length/Bond angle	X-Ray	MM2	
		cis-	*trans*-
Ti–N	2.141	2.125	2.118
Ti–N^1	2.141	2.143	2.127
Ti–O	1.835	1.867	1.823
Ti–O^1	1.835	1.848	1.832
Ti–Cl	2.346	2.349	2.348
Ti–Cl^1	2.346	2.356	2.348
O–Ti–O^1	113.3	76.71	110.2
N–Ti–N^1	76.1	79.25	80.14
Cl–Ti–Cl^1	168.7	81.59	168.9
O–Ti–N	85.4	76.71	84.13
O^1–Ti–N^1	85.4	91.68	85.48

Bond lengths are in Å. Bond angles are in degrees.

Table 2. Strain Energies Calculated for the *cis*- and *trans*-Conformers of the Ti Complexes[a)]

Complex	Steric energy (K cal/mol)		
		cis-	*trans*-
Ti(salen)Cl_2	Comp.	0.6302	0.5094
	Bend.	8.5830	2.6850
	Str. bend	−0.0742	−0.0057
	VdW.	7.2852	5.6492
	Torsion.	−11.1417	−11.1593
	Total energy	5.1770	−2.4886
Ti(salprn)Cl_2	Comp.	0.7220	0.5754
	Bend.	7.2833	2.8120
	Str. bend	−0.0304	−0.0667
	VdW.	9.470	7.1589
	Torsion.	−10.283	−10.4505
	Total energy	7.0282	−0.1064
Ti(salbuen)Cl_2	Comp.	0.3387	0.4232
	Bend.	5.4341	3.0772
	Str. bend	−0.0164	−0.0606
	VdW.	6.1439	7.5375
	Torsion.	−10.6959	−10.7321
	Total energy	1.1793	−0.8319
Ti(salpent)Cl_2	Comp.	0.3265	0.5092
	Bend.	5.0148	3.0439
	Str. bend	−0.0617	−0.1021
	VdW.	5.6254	6.2259
	Torsion.	−10.3050	−10.7565
	Total energy	0.4388	−1.2301
Ti(salhex)Cl_2	Comp.	0.5035	0.3569
	Bend.	5.8875	4.6204
	Str. bend	−0.0567	−0.0838
	VdW.	6.1840	6.7887
	Torsion.	−11.1111	−11.1499
	Total energy	1.2812	−0.6290

a) where Comp. is compression energy; Bend. is bending energy; Str. is stretch bend energy; vdW. is van der Waals energy; Torsion. is torsional energy.

Molecular Mechanics Calculations of Ti(Schiff-base)-Cl_2 Complexes. Force-field calculations have been performed for mononuclear Ti(IV) complexes of the Schiff-base ligands in both the *cis*- and *trans*-arrangements shown in Fig. 1. Using the X-ray structural parameters, the initial coordinates of the Ti(salen)Cl_2 has been generated. Complete optimization has been carried out on the structure by varying the force constant corresponding to the Ti–N and

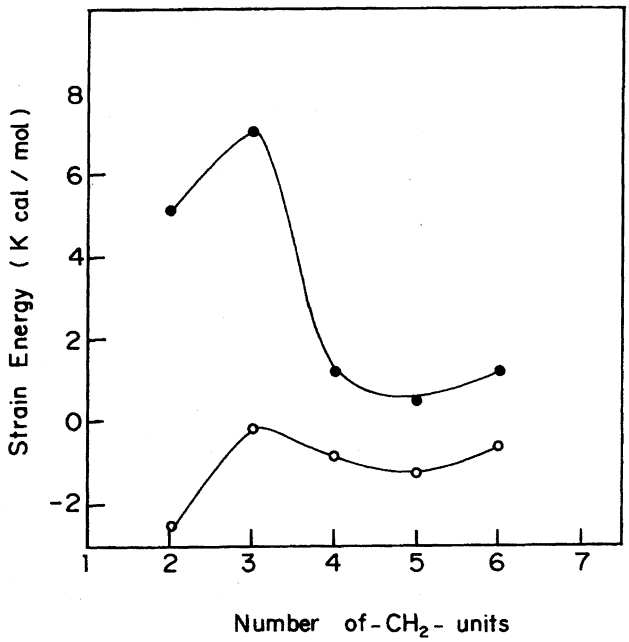

Fig. 2. Plot of total strain energy of the various titanium Schiff-base complexes in both *cis*- and *trans*-conformations as a function of number of $-CH_2-$units. *cis*- (●) and *trans*- (○).

Ti–O distances and the O–Ti–O, N–Ti–N, and O–Ti–N bond angles. The force constants corresponding to the minimum-energy conformer have been used for predicting the geometries of the other complexes investigated in this study. The force-field parameters corresponding to the Ti–N and Ti–O bond lengths are 1.9 mdyn $Å^{-1}$ and the angle bending force constants corresponding to the type O–Ti–O, N–Ti–O, and N–Ti–N is 0.3 mdyn rad^{-1}. The geometrical parameters corresponding to the minimum energy for the *cis*- and *trans*-arrangements of Ti(salen)Cl_2 are given in Table 1 along with the values obtained from X-ray crystallography. It can be observed from the table that *trans*-structure has now been predicted for Ti(salen)Cl_2. The close agreement between the calculated and X-ray data assures the quality of the force constants chosen for the present study.

The total strain energies calculated for Ti(Schiff-base)Cl_2 (where Schiff-base=salen, salprn, salbuen, salpent, and salhex) for both *cis*- and *trans*-arrangement are presented in Table 2. It can be observed from the total strain energy that *trans*-Ti(salen)Cl_2 is less strained compared to its *cis*-conformer. A similar trend can be observed in the strain energies of Ti(salprn)Cl_2 and Ti(salbuen)Cl_2. The negative total strain energies of the *trans*-conformations of Ti(salen)Cl_2, Ti(saplrn)Cl_2, Ti(salbuen)Cl_2, and Ti(salhex)Cl_2 indicate that the stabilization of these complexes is due to an attractive van der Waals interaction present. On the other hand, the stabilization of *cis*-Ti(salpent)Cl_2 arises due to a deviation of the structural parameters from the strain-free values. It can be observed from the table that *trans*-Ti(salen)Cl_2 is more stable when compared to other systems. The calculation revealed that since the difference in the total strain energies of the *cis*- and *trans*-Ti(salbuen)Cl_2, Ti(salpent)Cl_2, and Ti(salhex)Cl_2 is small, there is a possibility of the presence of the *cis*-conformer in the equilibrium mixture. A plot of the total strain energies of Ti(Schiff-base)Cl_2 complexes in both the *cis*- and *trans*-arrangements with a number of $-CH_2-$ units has been made, and is presented in Fig. 2. It can be observed from the figure that the *trans*-conformation is more favored when compared to the *cis*-arrangement. It is also interesting to observe that the variation in the total strain energy with the number of $-CH_2-$ units is similar for both the *cis*- and *trans*-conformation.

It is evident from the table that the *trans*-structure has been predicted for the mononuclear complexes of Ti(IV)(salen)-Cl_2 and Ti(IV)(salprn)Cl_2. In the case of Ti(IV) complexes

Table 3. Selected Bond Length and Bond Angle Parameters of the Various Ti(Schiff-base)Cl_2 Complexes Minimized for *cis*- and *trans*-Conformation

Bond Length/	Ti(salprn)Cl_2		Ti(salbuen)Cl_2		Ti(salpent)Cl_2		Ti(salhex)Cl_2	
Bond Angle	*cis*-	*trans*-	*cis*-	*trans*-	*cis*-	*trans*-	*cis*-	*trans*-
Ti–N	2.1435	2.1425	2.1411	2.1379	2.1415	2.1464	2.1467	2.1417
Ti–N^1	2.1437	2.1520	2.1313	2.1354	2.1417	2.1546	2.1533	2.1541
Ti–O^1	1.8665	1.8446	1.8446	1.8417	1.8415	1.8490	1.8542	1.8385
Ti–O^1	1.8700	1.8665	1.8539	1.8519	1.8510	1.8535	1.8564	1.8409
Ti–Cl	2.3502	2.3484	2.3500	2.2506	2.3498	2.3528	2.3540	2.3550
Ti–Cl^1	2.3545	2.3506	2.3476	2.3496	2.3469	2.3498	2.3469	2.3484
O–Ti–O^1	86.32	104.42	79.67	104.29	78.40	101.48	79.42	93.74
N–Ti–N^1	82.32	90.08	89.27	90.46	90.56	94.96	95.16	102.94
Cl–Ti–Cl^1	79.63	142.78	85.62	143.12	83.84	141.66	84.49	142.97
O–Ti–N	81.11	83.14	81.39	83.14	81.44	81.38	79.34	81.96
O^1–Ti–N^1	85.14	84.19	81.62	83.10	85.15	83.96	81.98	83.30
C=N	1.2841	1.2830	1.2862	1.2832	1.2861	1.2890	1.2896	1.2917
C=N'	—	—	1.2833	1.2846	1.2894	1.2845	1.2838	1.2865

Bond lengths are in Å. Bond angles are in degrees.

of salbuen, salpent and salhex, the total energy difference between the *cis*- and *trans*-conformers is not large enough for one to make definite predictions about the preferred conformation. In these compounds the total energy of the *trans*-conformer however is also lower than that of the *cis*-conformer. The geometrical parameters for the minimum-energy conformations of Ti(salprn)Cl_2, Ti(salbuen)Cl_2, Ti(salpent)Cl_2, and Ti(Salhex)Cl_2 have been calculated, and are presented in Table 3.

Proton NMR spectroscopy has proved to be an excellent tool for distinguishing the *cis*-isomer of M(Schiff-base)Cl_2 type complexes from the corresponding *trans*-isomer.[42] In the case of *cis*-Ti(Schiff-base)Cl_2 due to magnetic inequivalence, two signals for azomethine protons are expected, and the extent of separation between two HC=N chemical shifts is expected to be influenced by the degree of magnetic inequivalence. On other hand, for the *trans*-isomer only one signal for the azomethine proton is expected, since in this configuration the two azomethine protons are magnetically equivalent. In the case of the complexes investigated in this study there is no evidence for two distinct azomethine signals. The azomethine protons in the case of Ti(IV) complexes of salen, salprn, salbuen, salpent, and salhex complexes of salen, salprn, salbuen, salpent, and salhex appear at 8.60, 8.62, 8.76, 8.8, and 8.75 ppm respectively. This shows that at least in solution all of the compounds investigated in this study have a *trans*-dichloro geometry. These observation parallel the findings based on a molecular-mechanics calculation.

In the molecular-mechanics calculations we can correlate the relative stabilities of coordination compounds with the same ligand structure around the metal atom. The stability differences due to electronic effects are not explicitly included in the molecular-mechanics calculation. The choice of preferred conformer of the compounds investigated in this study is based purely on steric arguments. The electronic effects may also influence the preferred conformer. From this study, it can be observed that the steric interactions play a major role in the stabilization of the low-energy conformer.

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