Force field calculation on the structure of transition metal complexes: Application to Schiff-base complexes of Ti(IV)

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Force field methods have been successfully applied for the determination and prediction of chemical structures with special emphasis on peptides and nucleic acids. The force field calculations on transition metal complexes have posed some special difficulties. A large variety in coordination geometry and the ability of different metal ions to adopt more than one ligand environment make the force field parameterization for transition metal complexes difficult. The high symmetry of the coordination shell in the transition metal complexes leads to an additional constraint in their force field treatment which is not normally encountered in the case of organic compounds. For example, in the case of Ti(salen)Cl$_2$, there are two sets of chemically equivalent, N, O and Cl atoms. These atoms exhibit either 90 or 180° for N–Ti–O, Cl–Ti–O and Cl–Ti–N bond angles. This causes a multiple referencing problem in the force field treatment of transition metal complexes. To eliminate the multiple reference problem in the force field treatment, we have numbered the two chemically equivalent N, O and Cl atoms differently. Extensive reparameterization of the force fields in the MM2 program developed by Allinger and later modified by Endicott and his coworkers has now been made. A set of force field parameters has been refined through iterative approaches of minimization of strain energy and values obtained from experimental reference data. The reference values for the bond lengths have been taken from the X-ray structure of unstrained Ti(IV) complexes. Force constants have been optimized such that the predicted bond lengths, bond angles and torsional angles are in satisfactory agreement with those values observed in X-ray crystal structure. In this work, the optimized geometrical parameters for a homologous series of Schiff-base ligands of the general formulation OC$_6$H$_4$CH=N–(CH$_2$)$_n$–N=CH–C$_6$H$_4$O (where n = 1, 2, 3, 4, 5 and 6) and their Ti(IV) complexes have been presented. Total strain energies have been calculated for the *cis*- and *trans*-arrangements and some structural generalizations made.

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