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A Molecular Mechanics Model for the First Solvation Sphere of Complex Cations

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We have recently described our efforts to use molecular mechanics to investigate reaction profiles of some transition metal complexes [1]. In our approach, we factor the free energy of activation for the process of interest as:

$$\Delta G_{\mathrm{obs}} = \Delta G_{\mathrm{int}} + \Delta G_{\mathrm{strain}} + \Delta G_{\mathrm{CF}} + \Delta G_{\mathrm{solvation}} + \ldots$$

in which $\Delta G_{\mathrm{strain}}$, ΔG_{CF} and $\Delta G_{\mathrm{solvation}}$ are the strain energy, crystal field and solvation energy contributions to the observed free energy of activation, and ΔG_{int} is the hypothetical free energy of activation for the process independent of these environmental factors.

We have found reasonable agreement between experimental activation energies for aquation of a series of *trans*-dichloro(tetraamine)cobalt(III) cations and intramolecular strain energy estimates for the ground state and for proposed five coordinate intermediates. For a series of flexible tetraamine ligands, we calculate $\Delta G_{\mathrm{int}} = 123$ kJ mol^{-1}. For the analogous complexes with macrocyclic ligands, however, ΔG_{int} ranges from 133 to 139 kJ mol^{-1}, and does not vary systematically with either intramolecular strain energy estimates or with electronic structure parameters. Accordingly, we have sought a means to quantitatively estimate the contributions of solvation effects to the reactions of interest.

Solvation phenomenon have been of intense theoretical as well as practical interest [2–15]. We have been dissuaded from attempting to apply contemporary ***ab initio*** or Monte Carlo methods by the complexity of our target molecules. The series of complexes of immediate interest comprise 38 to 50 atoms and from 196 to 220 electrons, placing our problem – and others of similar magnitude – beyond the scope of contemporary quantum methods. We have, therefore, sought to apply molecular mechanics techniques to a model for the first solvation shell of the complexes of interest. In this preliminary report, we describe van der Waals molecules formed through the interaction of water with the *trans*-dichloro-(1,4,8,11-tetraazacyclotetradecane)cobalt(III) complex cation.

There is a striking similarity between the non-bonded potential functions of our semi-empirical force field model and those commonly employed in modelling solvation phenomena [2–4]. In particular, our van der Waals potentials closely resemble Jorgensen's TIP functions [5–15]. As a first approximation, therefore, we have represented the van der Waals potential of the solute as the aggregate of the non-bonded terms of one of our familiar complex cations. We chose the cationic complex *trans*-dichloro-(1,4,8,11-tetraazacyclotetradecane)-cobalt(III) to take advantage of several previous strain energy calculations which have established the validity of the force field model [1, 16, 17], and of the high symmetry of the cation (C_{2h}, in which the Cartesian octants are identical) which simplifies the search for local energy minima. We chose the best available van der Waals potential field model for water to represent the solvent.

We have now completed these calculations for some tems containing from one to fourteen independent water molecules. In our model, we locate water molecules at a reasonable distance (*ca.* 500 pm) from the complex using otherwise randomly chosen coordinates and orientations. All non-bonded distances less than 1000 pm are considered, and the energy of the system is minimized as usual [17], with the water molecules free to move to positions of minimum energy with respect to the 'solute' cation. We find that water molecules also rotate with respect to the cation to optimize van der Waals interactions. Eventually, however, the solvation shell begins to expand; we terminate the calculation when we detect a monotonic increase in water–cation distances. The energy minimized configuration for the first attempt is shown in Fig. 1.

We have now completed these calculations for some 80 sets of initial water coordinates. About one-third of the water molecules migrate away from the cation – we terminate the calculation when the closest contact between a water molecule and the cation

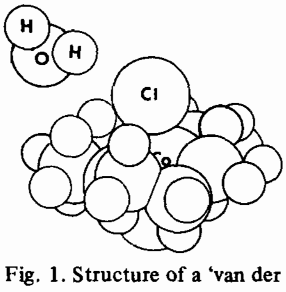

Fig. 1. Structure of a 'van der Waals' *trans*-dichloro-(1,4,8,11-tetraazatetradecane)cobalt(III)–water molecule.

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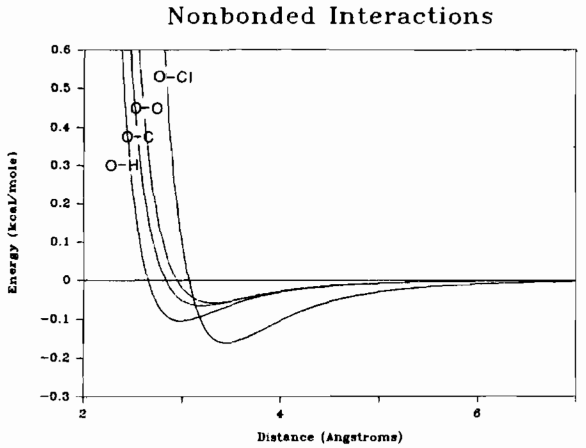

Fig. 2. van der Waals potentials as a function of internuclear separation (parameters from ref. 17).

exceeds 1200 pm – consistent with the extremely shallow van der Waals potential energy minima (Fig. 2). The water molecules which bind to the cation are found in intuitively satisfying locations. The water molecule shown in Fig. 1 is oriented with one proton about 390 pm from the chloride ion. The second proton is directed toward the solvent, and the oxygen atom is more or less between the protons of two adjacent methylene groups, consistent with the 'hydrophobic' effect described earlier [8, 10, 12, 13]. We anticipated this result since, in the absence of explicit coulombic terms in our potential functions, the complex is essentially a substituted hydrocarbon.

Positions of minimum energy for water molecules in the first solvation shell tend to cluster at the edge of the plane of the metal ion and nitrogen donors. These water molecules are arranged with the oxygen toward the ligand hydrocarbon residues. Few of the 80 trial water molecules find energy minima near the chloride ions, and none were found in the vicinity of the coordinated nitrogen atoms. Water molecules in the first solvation shell evidently are not randomly (*i.e.* not spherically) distributed about the complex.

We are now exploring methodology which will enable us to make reasonable estimates of dipolar contributions to intermolecular potential functions.

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