A Monte Carlo Study on a Magnesium Cyclen Complex

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Z. Naturforsch. **43a,** 797–800 (1988); received June 13, 1988

A Monte Carlo simulation has been performed to study the hydration of the magnesium complex of 1,4,7,10-tetraazacyclododecane (cyclen). An intermolecular potential function for magnesium cyclen complex and water, derived from ab initio calculations was used. The first hydration shell results to consist of 18 water molecules.

Introduction and Method

Several theoretical studies on 1,4,7,10-tetraazacyclododecane (cyclen) have already been performed in order to reveal enthalpic and solvation related effects contributing to macrocyclic effects and complex stability [1–7]. The hydration of the magnesium/cyclen complex [8] has been studied previously by means of a MC simulation based on the assumption of additivity of ion-water and complex-water potentials [9].

In this work, the analytical pair potential function between the magnesium cyclen complex and water was derived from full ab initio computations [10] on the complex/water energy surface:

$$\Delta E(W,C) = \sum_{i=1}^{3}\sum_{j=1}^{33}\left[-\frac{B_{ij}^{ab}}{r_{ij}^{6}} + \frac{A_{ij}^{ab}}{r_{ij}^{12}} + \frac{q_i q_j}{r_{ij}} \cdot \left(1 + \frac{C_{ij}^{ab}}{r_{ij}} + \frac{D_{ij}^{ab}}{r_{ij}^{2}}\right)\right], \quad (1)$$

where A_{ij}^{ab}, B_{ij}^{ab}, C_{ij}^{ab} and D_{ij}^{ab} are the fitted parameters and r_{ij} is the distance between an atom i of water (W) and an atom j of the complex (C), q_i and q_j are the net charges of atoms i and j (in atomic units) of the isolated molecules, obtained from the Mulliken population analysis [11]. For the water/water interaction, the MCY potential was used [12].

The Monte Carlo simulation, modified according to Metropolis et al. [13], has been performed under the same conditions and definition of the space regions (Fig. 1) as in [8]. The top region (T) is defined by a rotating 45 deg vector around the z axis above and below the molecular plane, the side region (S) contains all space outside this region, the plane region (P) denotes the space within $z = \pm 1.0$ Å, and the entire system (M) comprises the regions T and S. The basic cubic box contained one complex and 200 water molecules at 25 °C, 1 atm. The density was 1.00 g/cm^3. The box side length was 18.34 Å, and for the spherical cut-off half of the box side length was chosen.

Due to the enormous computational effort for the large system higher order potentials could not be considered for the complex-water interactions. As the much rougher assumption of additivity of ligand-

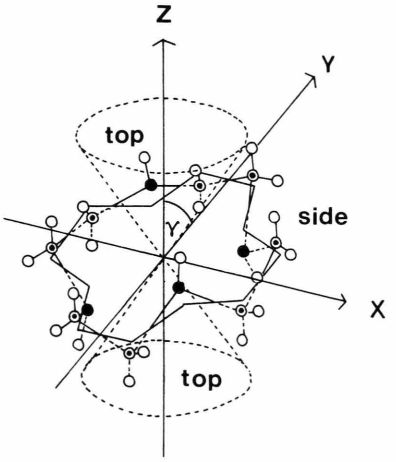

Fig. 1. Definition of regions around the Mg(II) cyclen complex ($\gamma = 45°$), ●:N, ⊙:C.

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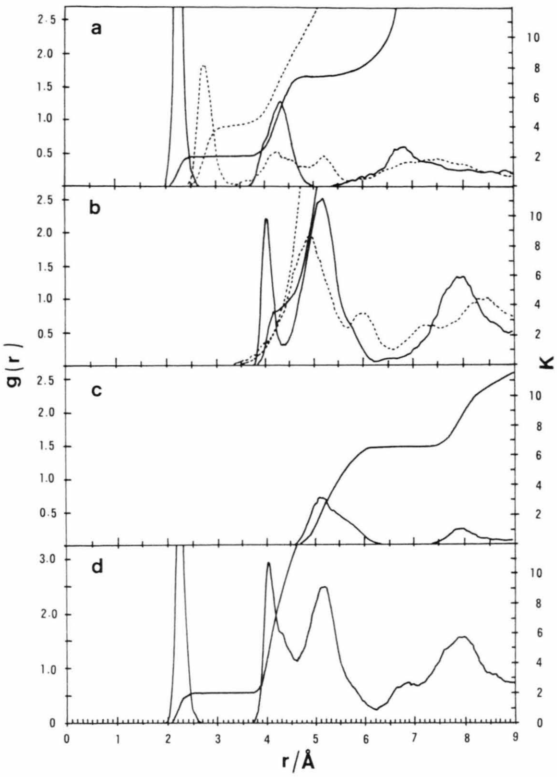

Fig. 2. Calculated Mg(II)-oxygen (——) and Mg(III)-hydrogen (– – –) radial distribution functions and running integration numbers for the top (a), side (b), plane (c) and entire system (d) regions of magnesium cyclen complex as defined in Figure 1.

water and ion-water potentials led already to reasonable results for the hydration structure [9, 10], restriction to pair potentials in this work seemed to be justified.

Results and Discussion

The positions of the 200 water molecules used as initial configuration for starting the simulation were taken from the last step of the previous simulation (see [8]). Due to this suitable initial configuration, the energy of the system quickly converged. The simulation was carried out for another 1.6×10^6 configurations, and the last 1.5×10^6 configurations were used for data evaluation.

From the radial distribution functions, corresponding coordination numbers and the angular distribution of the water molecules with respect to the central Mg(II) ion were obtained.

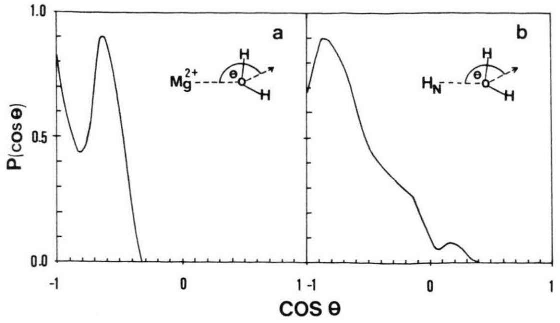

Fig. 3. a) Distribution of cos θ for the top region ($r_m = 2.7$ Å) and b) near H_N.

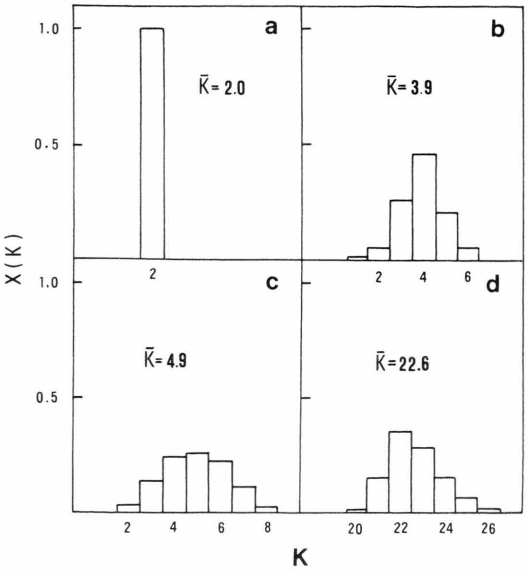

Fig. 4. Distribution of coordination numbers KO around the magnesium ion for the following regions: (a) top ($r_m = 2.7$ Å), (b) top ($r_m = 3.6-5.1$ Å), (c) side ($r_m = 4.4$ Å) and (d) $Z = 3.0$ Å.

The first peaks of the radial distribution functions $g_{TO}(r)$ and $g_{TH}(r)$ in Fig. 2a reflect the two waters located at $x = y = 0$, $z = \pm 2.2$ Å, with the coordination number $K_{TO} = 2$ for water oxygen and $K_{TH} = 4$ for water hydrogen atoms. These two waters point with their oxygen atoms towards the magnesium ion. The angular distribution shown in Fig. 3a indicates highest populations at $\theta = 130°$ and $180°$, proving lone-pair and dipole orientations as almost equivalent, in contrast to the result based on additive potentials which strongly favoured the dipole configuration (8). The exclusive coordination number of water oxygen atoms $K_{TO} = 2$ at $r_m = 2.7$ Å (Fig. 4a) indi-

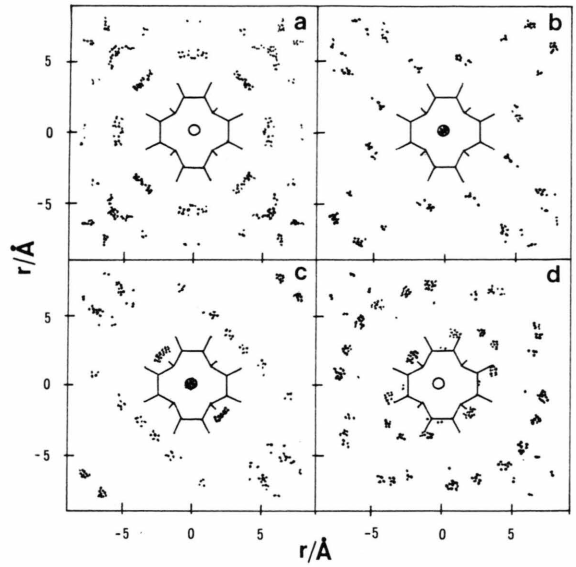

Fig. 5. Distribution of water in strata parallel to the plane of the magnesium cyclen complex within ± 0.2 Å of selected z values (a) $z = 0.0$ Å, (b) $z = 2.0$ Å, (c) $z = 2.5$ Å, (d) $z = 3.0$ Å.

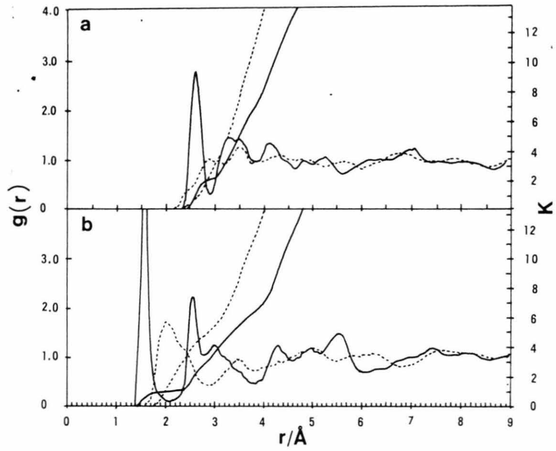

Fig. 6. Calculated atom-oxygen (——) and atom-hydrogen (---) radial distribution functions and running integration numbers for an (a) N and (b) H_N atom of cyclen.

cates strong binding of these two waters. The probability distributions illustrated in Figs. 5b and 5c confirm the locations of those two waters within 1.8 to 2.7 Å in the z-axis, one above and one below the $x\,y$ plane of the complex.

The second peak of $g_{MO}(r)$ (Fig. 2d) is a combination of the second peak of $g_{TO}(r)$ (Fig. 2a) and the first peak of $g_{SO}(r)$ (Fig. 2b) which contains eight metal ion oriented water molecules; four (type 2a) belong to the top region and another four (type 2b) to the side region. The second peak of $g_{MO}(r)$ and the first peak of $g_{SO}(r)$ actually represent an averaged coordination number of $\bar{K}_0 = 3.9$ (at $r_m = 3.6-5.1$ Å, Fig. 4b) and $\bar{K}_0 = 4.9$ (at $r_m = 4.4$ Å, Fig. 4c). The distribution of coordination numbers indicates a wider variation and hence an easy exchange.

The 2a waters (Fig. 2a) contained in the second peak of $g_{TO}(r)$ are 4.3 Å far from the magnesium ion and about 3.0 Å above/below the $x\,y$ plane (cf. probability plot of Fig. 5d).

The 2b waters are located 4.0 Å far from the magnesium ion and opposite to the respective 2a water on the other side of the $x\,y$ plane, also about 3.0 Å above/below the $x\,y$ plane (as visible in Fig. 5d).

The second peak of $g_{SO}(r)$, at $r_m = 4.4-6.3$ Å contains approximately twenty two water molecules (indicated by $\bar{K}_0 = 22.6$, Fig. 4d), but only eight waters of these belong to the first hydration sphere. This becomes evident by comparison with Fig. 2c (plane region), where these waters appear as the first peak (coordination number approx. 7), and with Fig. 6a, which indicates every nitrogen to be associated with 2 waters.

They are defined as water of type 3, and are located between the H_2C groups, close to the $x\,y$ plane (cf. Fig. 5a). The other water molecules of this peak belong to the second solvation shell.

The first peak of $g_{PO}(r)$ (Fig. 2c) shows the waters of type 3 to be located 5.2 Å far from magnesium ion. The first peak of $g_{NO}(r)$ (Fig. 6) which belongs to waters 3, shows that these waters are coordinated to the H_N atoms of cyclen via hydrogen bonds (N ... O = 2.6 Å). The dipole moment orientation of these waters with respect to N atoms of cyclen with $\theta \sim 145°$ (Fig. 3b) shows that four of these waters (also confirmed by the first peak of $g_{H_NO}(r)$, Fig. 6b) are bound to N–H atoms of cyclen via slightly nonlinear hydrogen bonds (N–H ... O). Therefore, summing up all water molecules to be attributed to the first hydration shell of the complex (types 1, 2a, 2b and 3), we obtain a total of eighteen.

The further waters appearing as the third peaks of $g_{SO}(r)$ and $g_{MO}(r)$ (Fig. 2b and 2d) probably represent secondary hydration spheres, located within 5.0–8.0 Å in the side and top regions, respectively. Due to box-size and cut-off of the interaction potential these third peaks of $g_{TO}(r)$ and $g_{SO}(r)$ cannot be considered too reliable. We can therefore just conclude that a loosely-bound second hydration sphere is likely to exist.

Comparing the results of this study, performed with a fully-evaluated ab-initio pair potential function, with the results of previous work based on the additivity assumption of ion-water and ligand-water interactions, it can be concluded that such simplified approaches can already give a reasonable qualitative picture of the hydration structure. Details however, as e.g. the orientation of water molecules, should not be expected to be always correct and will need the implementation of a separately evaluated complex-water potential function.

Acknowledgement

Generous supply of computer time by the Computer Centre of Innsbruck University is gratefully acknowledged.

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