Electronic Supplementary Information for Dalton Transactions

Synthesis, complexation and NMR relaxation properties of the conformation-switching Gd^{3+} complexes of $Mes(DO3A)_3$

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Electronic Supplementary Information

Simple molecular mechanics studies have been performed to evaluate different theoretical structures for $[Mes\{DO3A\}\{Gd(DO3A)(H_2O)\}_2]^{3-}$. All calculations were performed using Scigress Explorer Ultra Version 7.70.47 (Fujitsu Ltd) and the classical MM3 force field. Gd^{3+} ions have been replaced by Y^{3+} having the same ionic radius. The $[Mes\{DO3A\}\{Y(DO3A)(H_2O)\}_2]^{3-}$ complex was embedded into a drop of water consisting of 393 H_2O molecules (Fig. S1 (a)). Convergence was supposed to be attaint for an energy gradient < 10^{-5} kcal/mol.

The first structure minimized is shown in Fig. 1(b) (only bulk water molecules are not shown for clarity). The structure corresponds to that proposed in our paper (Scheme 3(b)) : Two carboxylates from the uncomplexed DO3A-unit bind to two different Y^{3+} ions on the two other DO3A. Each Y^{3+} ion has one water molecule in the first coordination sphere. This structure corresponds to the lowest energy of all minimized structures (-2363 kcal/mol).

The second structure (Fig. 1 (c)) was obtained by starting with a configuration with two carboxylates bound to the same Y^{3+}. The second Y^{3+} has two water molecules in the first coordination sphere (structure proposed by one of the referees). This structure could only be minimized by introducing a weak bond (“hydrogen bond”) between the ion and a carboxylate oxygen. The energy of this conformation is 481 kcal/mol higher than that of Fig. 1 (b).

The conformation shown in Fig. 1 (d) is obtained by deleting the weak Y^{3+}-O bond introduced in Fig. 1 (c) followed by energy minimization. One of the two carboxylates leaves the first coordination sphere of the Y^{3+}. The energy of conformation 1 (c) is 288 kcal/mol higher than that of 1 (a). If the second weak bond is also deleted the carboxylate stays in the first coordination sphere but the energy decreases again and the difference to 1 (a) is now +98 kcal/mol.

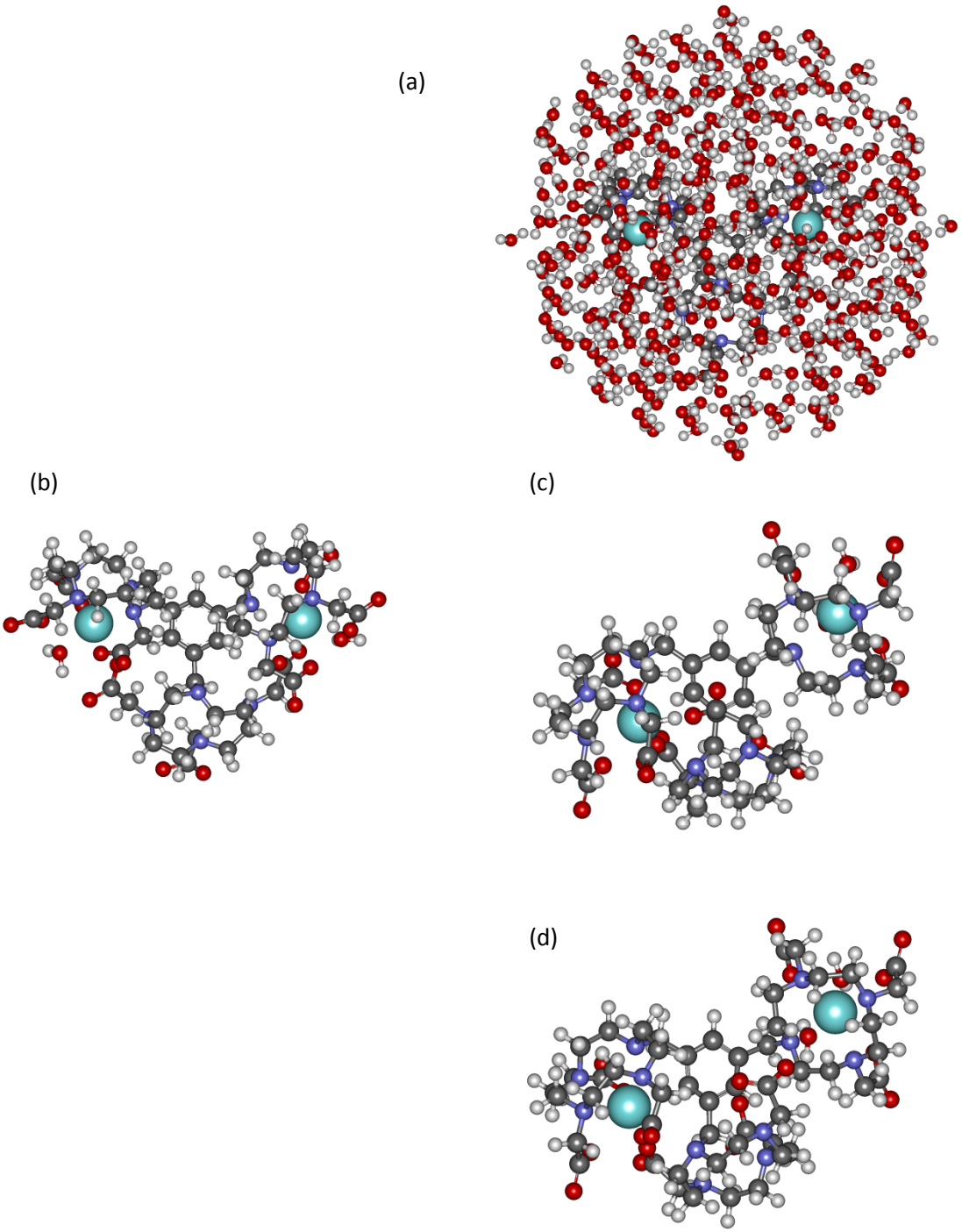

Figure S1 Structures of $[Mes\{DO3A\}\{Y(DO3A)(H_2O)\}_2]^{3-}$ from molecular mechanics using MM3 force field. All structures have been minimized in a drop of 393 water molecules (a)